U. S. DEPARTMENT OF COMMERCE

# BUREAU OF STANDARDS JOURNAL OF RESEARCH

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# A METHOD FOR DETERMINING THE CHANGE IN TRANSFERENCE NUMBER OF A SALT WITH CHANGE IN CONCENTRATION. A MODIFICATION OF THE MOVING BOUNDARY METHOD

By Edgar Reynolds Smith

ABSTRACT

A method for determining the rate of change of the transference number of a salt with change in concentration, based on a modification of the moving boundary method, is described. Junctions between solutions of the same salt at different concentrations are formed and the volumes through which the junctions move during the passage of known amounts of electricity are measured. The changes in transference numbers between the concentrations across the junctions are calculated from these data. The method was tested for solutions of lithium, sodium, and potassium chloride. It was found that potassium chloride exhibits but little change in transference number on passing from dilute to 4.7 molal solution.

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## I. NOTATION

$C$, concentration in moles per cubic centimeter.
$M$, concentration in moles per 1,000 gs of water.
$T_R$, transference number of ion constituent $R$.
$T'_R$, $dT_R/dC$.
$i$, current density.
$F$, 96,500 coulombs.
$t$, time.
$x$, distance.
$V$, volume.
$Q$, $\int \frac{i}{F} dt$.
$U$, cation mobility.
$W$, anion mobility.
$E$, electrical potential.
$l$, specific conductance.

## II. INTRODUCTION AND THEORY

When a current of electricity is passed through a solution of an electrolyte the concentration of which varies from point to point, there will, in general, be an accompanying shift in the concentration at

every point, due to the well-established fact that ion mobilities are functions of the concentration. In what follows, the flow of electricity is considered to be unidirectional through a cylindrical tube of constant cross section having electrodes so far removed from the portion under consideration that changes in concentration resulting from the electrode reactions do not enter that portion. Also the effects of diffusion are neglected, or rather eliminated, since the prevention of diffusion by the action of the electric current is one of the necessary conditions for the measurement of transference numbers by the moving boundary method. The general equations governing concentration shifts during electrolysis were developed some time ago by Kohlrausch.[1] For the simple case of a single uniunivalent electrolyte, $C^+A^-$, in aqueous solution the desired equations may be obtained as follows:

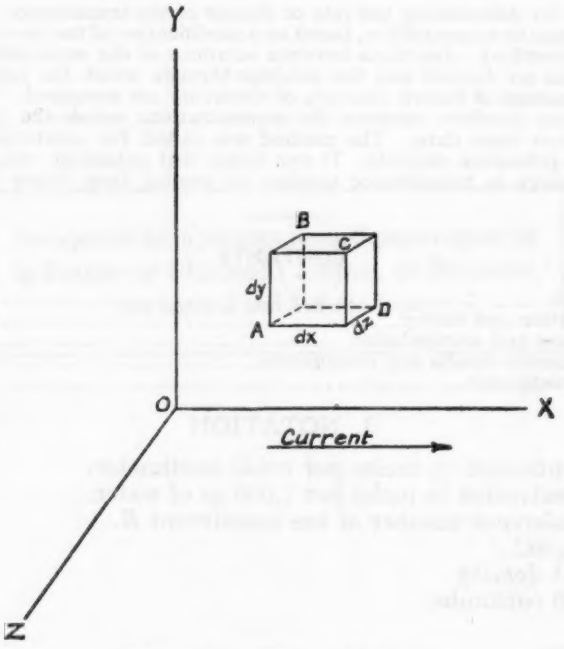


FIGURE 1.—*Element of volume*

Consider an element of volume $dv = dx\ dy\ dz$ in the solution. (Fig. 1.) The number of cations entering the face $AB$ in the time $dt$ is

$$N_{AB} = U\frac{dE}{dx}C\ dy\ dz\ dt = \frac{i}{F}T_c\ dy\ dz\ dt$$

Since

$$dE/dx = i/l = i/CF(U+W)$$

and

$$U/(U+W) = T_c$$

[1] F. W. Kohlrausch, Ann. Physik, **62**, p. 209; 1897.

while the number of cations leaving the element through the face $CD$ is

$$N_{CD}=\frac{i}{F}T_c\,dy\,dz\,dt+\frac{i}{F}\frac{\partial T_c}{\partial x}\,dx\,dy\,dz\,dt$$

The rate of increase in concentration is therefore

$$\frac{\partial C}{\partial t}=-\frac{i}{F}\frac{\partial T_c}{\partial C}\frac{\partial C}{\partial x}\text{ or }\frac{\partial C}{\partial Q}+T'_c\frac{\partial C}{\partial x}=0 \qquad (1)$$

since

$$\partial C/\partial t=(N_{AB}-N_{CD})/(dx\,dy\,dz\,dt)$$

The integral of equation (1) in terms of an arbitrary function $\phi$ is

$$C=\phi\,(x-T'_cQ) \qquad (2)$$

as can be shown by differentiation of this integral to obtain equation (1). Initially the concentration is a known function of the position; that is, $C=\psi\,(x)$ when $Q=0$, a condition which determines the nature of the function $\phi$. Therefore equation (2) becomes

$$C=\psi\,(x-T'_cQ) \qquad (3)$$

A junction between two solutions of the same salt at two different concentrations $C_1$ and $C_2$ can be considered as a region of continuous, even if rapid, change in concentration between $C_1$ and $C_2$. Observations on the motion of such a junction will, therefore, give information on the nature of $T'$ between the two concentrations.

The stability of boundaries of this type is probably connected with the space charge resulting from the variation in potential gradient across the junction. From Poisson's equation, $-d^2E/dx^2=4\pi\sigma/D$ where $\sigma$ is the space density of electric charge and $D$ is the dielectric constant, it is clear that such a space charge must exist at the junction, forming an electric double layer which tends to preserve the discontinuity between the two solutions. When the current is reversed the sign of the double layer also reverses and the junction remains stable for either direction of the current. The following cases are of interest:

1. The transference number of the salt is constant. In this case $T'=0$, and the concentration everywhere retains its initial value of $\psi\,(x)$. As many ions of each kind must enter the junction from one side as leave it from the other and the junction remains stationary.

2. The transference number is a linear function of the concentration. In this case $T=a+kC$ and $T'=k=$constant. Then $C=\psi\,(x-kQ)$. The junction moves with a velocity of $k\cdot i/F$ as can be seen from equation (1). Therefore, a measurement of the velocity of the junction under the influence of a known current density will give $dT/dC$ for the electrolyte.

3. The variation of transference number with the concentration is nonlinear. $T=f(C)$, $C=\psi\{x-f'(C)\cdot Q\}$, and at each instant the concentration condition at any point moves with a velocity of $if'(C)/F$. The usual type of this variation is illustrated in Figure 2 for lithium chloride and sodium chloride, the data being taken from

International Critical Tables.[2] It is seen from the figure that $T'$ is negative and a junction between any two concentrations should remain sharp and travel in a direction opposite to the direction of the current. A simple equation for calculating the transference number in such a case can easily be derived by reference to Figure 3. Let $\Delta V$ = the volume through which the junction moves when $Q$ equivalents of electricity are passed and $\Delta N$ = the increase in number of equivalents of salt in the volume $\Delta V$ accompanying the passage of the electricity. Suppose the junction moves down the tube while

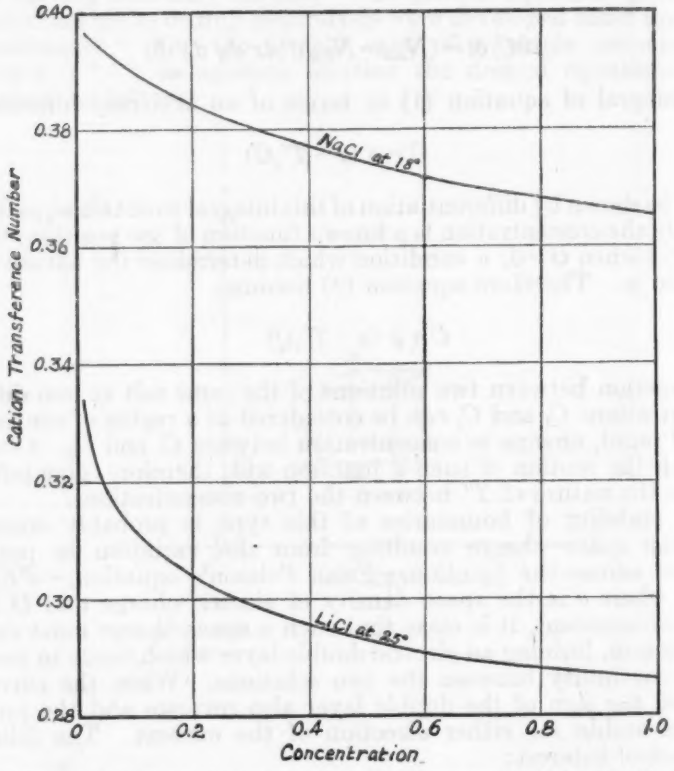


FIGURE 2.—*Transference numbers of lithium and sodium chlorides*

the current moves up through the solutions. Then $\Delta N = \Delta V(C_1 - C_2)$ and $\Delta N = \Delta N_C = \Delta N_A$ for electric neutrality. Therefore, $\Delta N_C = \Delta V \cdot (C_1 - C_2)$. Also $\Delta N_C = Q(T_1 - T_2)$. Solving for $(T_1 - T_2)$ gives

$$(T_1 - T_2) = \frac{\Delta V(C_1 - C_2)}{Q} \text{ or } \Delta T_c = \frac{\Delta V \cdot \Delta C}{Q} \tag{4}$$

If the transference number should happen to go through a maximum or a minimum value between the concentrations $C_1$ and $C_2$ on opposite sides of the junction, the motion becomes more complicated. For example, in Figure 4 at the left-hand limit of the junction

[2] Int. Crit. Tables, 6, p. 310, McGraw-Hill Co., New York; 1929.

where the concentration is $C_1$, $f'(C)$ is positive and the motion will be in the direction of the current, while at the right-hand limit where the concentration is $C_2$ and $f'(C)$ is negative the motion will be opposite to the direction of the current. thus, with the current flowing from $C_1$ to $C_2$, the junction tends to sharpen. Now, if the transference numbers $T_1$ and $T_2$ are nearly the same a slight adjustment in concentration by the action of the current might change the sign of the direction of motion of the junction by changing the sign of $\triangle T$ across the junction. Such an adjustment might take place if the current were stopped for a moment and then reversed. The junction, instead of reversing its motion with current reversal, might continue to move in the same direction as before.

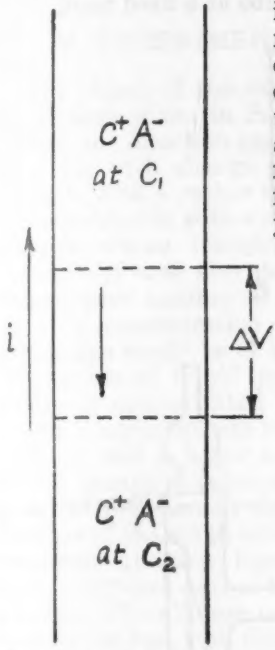


FIGURE 3.—*Moving junction between two salts*

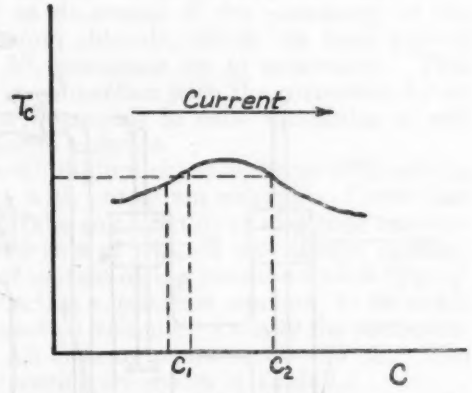


FIGURE 4.—*Variation of transference number with concentration*

## III. APPARATUS AND MANIPULATION

The transference cell is shown in Figure 5. The anode consisted of a piece of platinum gauze rolled into a cylinder and coated electrolytically with silver. The cathode was prepared in the same way, but with an additional coating of silver chloride and was immersed in precipitated silver chloride. The reservoir $G$ was used in filling the right-hand side of the apparatus with the more concentrated solution, including the junction tube $T$, which had an inside diameter of approximately 0.4 cm. The electrode tube $A$ and the tube $H$ were filled with the less concentrated solution. The method of separating the solutions at the start by means of the plunger $F$ has been described in another paper.[3] After the junction had been formed, with the current flowing, it was pulled down the tube $T$ to any suitable reading point on the scale $S$. This operation was carried out by opening stopcocks $D$ and $C$ while $E$ was closed thus withdrawing solution from the left-hand side. For this purpose the tube $I$, partly capillary

[3] E. R. Smith, J. Am. Chem. Soc., **50**, p. 1904; 1928.

at the open end and carrying the stopcock $C$, extended over the front side of the thermostat. When the junction had reached a suitable position, stopcock $D$ was shut, thus making the right-hand side of the apparatus tightly closed by ground-glass joints. The measuring tube $T$ was calibrated with mercury for volumes compared with readings on the glass scale $S$ which was attached to the tube at a fixed mark.

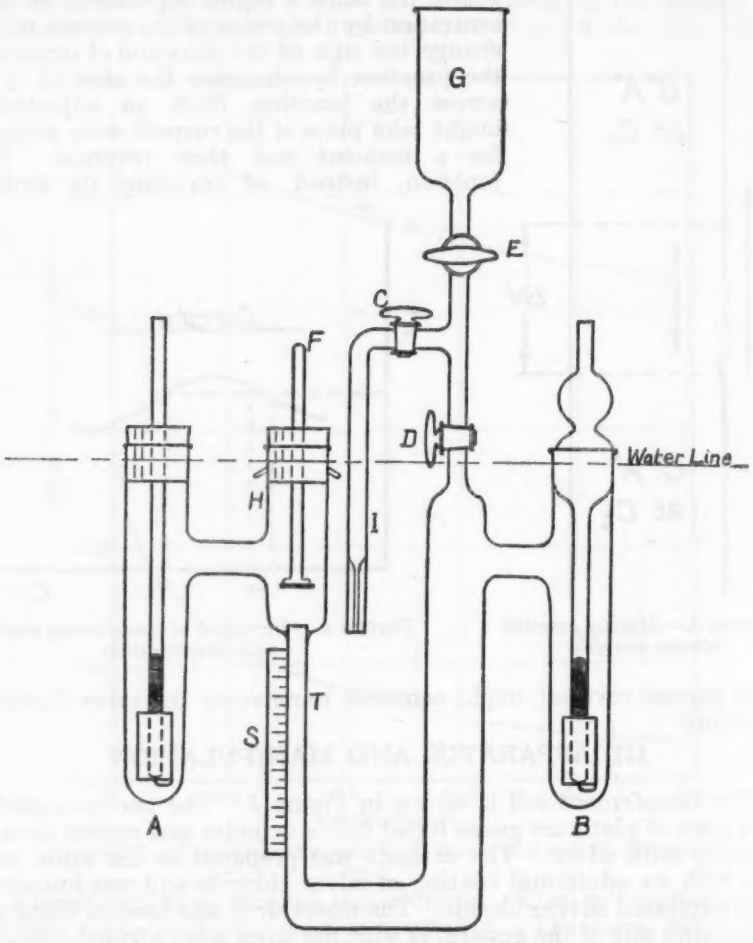


FIGURE 5.—*Transference cell*

The apparatus was immersed in a small water thermostat having plate glass front and back and provided with a stirrer, heater, and mercury contact regulator which held the temperature constant at $25° \pm 0.05$.

The quantities of electricity used were measured with a small copper coulometer consisting of a central cathode of heavy copper wire surrounded by a cylindrical sheet of copper in a beaker of 150 ml capacity. The order of magnitude of the cathode current density was 0.01 amp./cm.$^2$

The salts used were of "c. p." quality and were not tested or subjected to any further purification process. The solutions were prepared by weighing the proper quantities of salt and water to obtain the desired concentrations in terms of formula weights of salt per 1,000 g of water.

## IV. EXPERIMENTAL RESULTS AND CONCLUSIONS

The object of the experimental work was to test the theory and conclusions given in Section II and to develop a rapid method for finding the direction and rate of variation of the transference number of a salt with change in concentration. For this purpose, lithium chloride with a rather rapid rate of change of transference number, sodium chloride with a moderate rate of change (fig. 3), and potassium chloride whose transference number is practically constant were chosen. It was also desired to determine if the constancy of the transference number of potassium chloride, which has been proved up to a concentration of 2 $N$[4], continues up to saturation. This knowledge would be of value in connection with the correction for or elimination of liquid junction potentials in cells containing a salt bridge of concentrated potassium chloride.

One experiment was made with lithium chloride, three with sodium chloride, and a larger number with potassium chloride. Correction for the change in volume due to the combination of electrode reaction and ion migration in the closed side of the cell was always applied. Because of the small volume of motion of the junction in this type of measurement the volume correction sometimes amounts to as much as 50 to 100 per cent of the measured volume. Usually the correction was from 10 to 30 per cent. All measurements were at 25° C. The data for the test with lithium chloride are shown in Table 1.

TABLE 1.—*Junction between lithium chloride solutions of concentrations 0.1 and 0.2 mole per 1,000 g of water*

| Time (in minutes) | Cu deposited in coulometer | 1/Q | Corrected volume of motion of junction | $C_1\times10^3$ | $C_2\times10^3$ |
|---|---|---|---|---|---|
| | *g* | | *cc* | | |
| 80 | 0.0346 | 919 | 0.107 | 0.0995 | 0.1987 |

According to Figure 2, $dT_{Li}/dC = T'_{Li}$ is negative, and the theory requires that the junction move in the opposite direction to the direction of the current. This was found to be correct experimentally. From equation (4) and the data given in Table 1

$$\Delta T_{Li} = T^{0.1}_{Li} - T^{0.2}_{Li} = 0.107 \times 0.0992 \times 10^{-3} \times 919 = 0.00976 \qquad (5)$$

The values given in International Critical Tables, which are taken from the electromotive force measurements on lithium chloride concentration cells by MacInnes and Beattie[5] are $T^{0.1}_{Li} = 0.311$ and

[4] D. A. MacInnes (private communication).
[5] D. A. MacInnes and J. A. Beattie, J. Am. Chem. Soc., **42**, p. 1117; 1920.

$T_{Li}^{0.2}=0.304$. If the latter is taken as a reference value and substituted in equation (5), the value obtained in this experiment for $T_{Li}^{0.1}$ will be $0.304+0.00976=0.314$ which is an approximate agreement. On reversing the current, the boundary reversed its direction of motion, and although the amount of electricity passed in the reverse direction was measured only roughly from the time and readings of a milliammeter, the agreement was equally satisfactory.

The data for the test with sodium chloride are given in Table 2. In each case with sodium chloride the junction moved in the predicted direction, against the current, reversed with reversal of current and afforded values of $\Delta T_{Na}$ in substantial agreement with the gravimetric values at 18°.

TABLE 2.—*Junctions between solutions of sodium chloride*

| | Experiment No. | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| $M_1$ | 0.1 | 0.2 | 0.5 |
| $M_2$ | .2 | .5 | 1 |
| $t$ (minutes) | 68 | 45 | 40 |
| Cu deposited in coulometer | .0415 | .0409 | .040 |
| 1/Q | 766 | 777 | 795 |
| Corrected volume | .031 | .027 | .02 |
| $C_1\times10^3$ | .0995 | .1987 | .494 |
| $C_2\times10^3$ | .1987 | .4941 | .970 |
| $\Delta T_{Na}$ | .0024 | .0062 | .010 |
| $\Delta T_{Na}$ at 18° (Int. Crit. Tables) | .005 | .011 | .01 |

The experiments with potassium chloride can be divided into two groups. The first group, given in Table 3, was carried out with solutions in the concentration range of 0.05 to 1 molal where $T_K$ is known to be practically constant. In these experiments the motion of the junction was in every case opposite to the direction of the current and reversed when the current was reversed. This would indicate a negative sign for $dT_K/dC$. However, the junction shifts were small, and the somewhat uncertain correction for the volume changes at the electrode amounted to a considerable fraction of the measured shift. In view of these facts the results are in excellent agreement with the known constancy of the transference number of potassium chloride in the measured range of concentration.

TABLE 3.—*Junctions between potassium chloride solutions having concentrations up to 1 molal*

| | Experiment No. | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| $M_1$ | 0.05 | 0.1 | 0.2 | 0.4 | 0.2 |
| $M_2$ | .1 | .2 | .4 | .7 | 1.0 |
| $C_1\times10^3$ | .04980 | .09943 | .1983 | .3944 | .198 |
| $C_2\times10^3$ | .09943 | .1983 | .3944 | .6844 | .990 |
| $t$ (minutes) | 90 | 65 | 35 | 35 | 51 |
| g Cu plated in coulometer | .0430 | .0450 | .0278 | .0376 | .039 |
| 1/Q | 739 | 706 | 1,143 | 845 | 813 |
| Corrected volume (ml.) | .033 | .019 | .007 | .001 | .00 |
| $\Delta T_K$ | .0012 | .0013 | .0016 | .00025 | .003 |
| 100 $\Delta T_K/T_K$ (per cent) | .25 | .27 | .32 | .05 | .6 |

TABLE 4.—*Junctions between potassium chloride solutions having concentrations of from 1.0 to 4.7 molal*

| | Experiment No. | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| $M_1$ | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| $M_2$ | 1.5 | 2.0 | 3.0 | 4.0 | 4.7 |
| $C_1 \times 10^3$ | .969 | .969 | .969 | .969 | .969 |
| $C_2 \times 10^3$ | 1.433 | 1.883 | 2.742 | 3.551 | 4.088 |
| $t$ (minutes) | 27 | 28 | 25 | 24 | 30 |
| g Cu plated in coulometer | .0347 | .0381 | .0361 | .0351 | .0433 |
| $1/Q$ | 916 | 834 | 880 | 906 | 734 |
| Corrected volume (ml.) | .002 | .005 | .003 | .002 | .006 |
| $\Delta T_K$ | .00085 | .0038 | .0047 | .0046 | .014 |
| $100\Delta T_K/T_K$ (per cent) | .17 | .78 | .96 | .94 | 2.8 |

The second group of experiments with potassium chloride was carried out with 1 $N$ potassium chloride as the reference solution for the purpose of determining if the transference number remained practically constant from 1 $N$ up to saturation. Table 4 contains the data for this group. In all these experiments with the more concentrated solutions the current was passed from the more concentrated to the 1 molal solution and the junctions shifted slightly in the direction of the current indicating a positive value for $dT_K/dC$. In experiment 1 the junction reversed its direction when the direction of the current was reversed, but in the others the following peculiarities were noticed. In experiments 2 and 4 the junction remained stationary when the current was passed in the reverse direction, indicating a constant transference number. In experiments 3 and 5 the junction continued at about the same rate without changing its direction when the current was reversed. These peculiarities are hard to explain quantitatively, but it is possible that in such concentrated solutions complex formations may be a disturbing factor causing the apparent transference number to pass through a slight maximum or minimum value, so that a small concentration adjustment on either side of the junction changes the sign of $\Delta T$ across the junction. This same phenomenon was encountered with a junction between 0.05 and 0.2 molal potassium chloride solutions, but was not observed between 0.05 and 0.1 or between 0.1 and 0.2 molal solutions. If the effect is due to a slight maximum or minimum it would be expected to disappear on changing one of the concentrations. However, the results indicate that there is but little change in the transferene number of potassium chloide in going from dilute to the saturated solution.

A more extensive study of the behavior of junctions of this type is planned, including an experimental determination of the actual volume changes occurring in the electrode portions. The results obtained in this investigation are to be considered as a preliminary survey to test the theory and practicability of such measurements.

## V. ACKNOWLEDGMENT

The author desires to express appreciation to E. W. Washburn, chief chemist of this bureau, for many helpful suggestions and advice during the course of this work and to D. A. MacInnes and L. G. Longsworth, of the Rockefeller Institute for Medical Research, for valuable discussion and criticism.

WASHINGTON, March, 26, 1931.

# CARPET WEAR TESTING MACHINE

By H. F. Schiefer and A. S. Best


## ABSTRACT

A machine for testing the resistance to wear of carpets and similar floor coverings when they are subjected to definite wearing forces under controlled conditions has been developed at the National Bureau of Standards. The forces are chosen to produce the bending, slipping, twisting, and compression of the pile which takes place when a carpet is walked upon.

A circular sample of the carpet to be tested is tacked on a turntable which is brought to bear against two leather-covered wheels. One of the wheels is driven by a motor and in turn drives the turntable. The other wheel is used as a brake to produce slipping of both wheels on the carpet as it rotates. A vacuum cleaner removes the material which is worn off. The wear on the carpet is produced by a downward force, a horizontal stress and a slight twisting motion. They have definite values and may be varied. The rate of wear is evaluated by measuring the change in thickness of the pile of the carpet with a sensitive thickness gage as the test proceeds.

The machine can be used to test the relative durability of carpets under definitely specified conditions. Whether the results are a satisfactory measure of probable relative durability of carpets in service has not been determined. The machine should be useful for studies of the effect of various factors on carpet wear and for studies of the relation between the composition and construction of carpets and their resistance to wear.


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## I. INTRODUCTION

Carpets and similar floor coverings are expected to be not only attractive in appearance and feel, but to be resistant to wear. The user of carpets is interested in the relative durability of the different types, and the manufacturer should know the relative durability of carpets of various compositions and constructions in order better to meet the varying requirements of his customers.

Practical service tests of carpets are expensive, time consuming, and difficult to control. Yet no one laboratory test can simulate all of the conditions to which carpets may be subjected in service. For these reasons, it was considered advisable as a first step in the study of

carpet wear to devise a machine in which samples of carpet could be subjected to definite wearing forces that may be varied at will under controlled, reproducible conditions.

This paper describes such a machine [1] and gives the results of some tests made with it. The reproducibility of the results is demonstrated and the effect of varying the applied forces is shown.

Under ordinary service conditions much of the wear of carpets appears to be caused by walking. In the act of walking the applied force is usually in a forward direction at the beginning of the step. It changes gradually through a vertical to a backward direction at the end of the step. In addition, walking is often accompanied by a slight horizontal rotary motion of the foot. The horizontal component of the initial foward force bends the pile of the carpet forward, while its vertical component compresses the pile. Toward the end of the step, the applied force tends to increase the bending of the pile yarns and to push them backward. Throughout the step there is a certain amount of slippage between the shoe and the carpet, first forward and then in the reverse direction. The horizontal rotary motion tends to twist the pile yarns and thus to increase the stresses on the fibers. As a result of this bending, slipping, twisting, and compression of the pile the fibers are gradually weakened, broken off, or pulled out of the base of the carpet.

The wear of carpets under certain conditions of service may be attributable to other causes. An accumulation of gritty material in a carpet may abrade and cut the fibers. Excessive use of cleaning devices may result in unnecessary wear. Impact forces may be one of the causes of the rapid wear of carpets on stairways. Atmospheric influences, such as very low or very high humidity or injurious fumes, may contribute to the wear of carpets in certain localities or under certain conditions of use.

These considerations led to the construction of a machine capable of subjecting small samples of carpet repeatedly to the wearing forces which appear to predominate when carpets are walked upon, namely, downward, horizontal, and twisting stresses with slippage. The machine is arranged so that the magnitude of these forces is known and can be varied. The material worn from the carpet during the test is removed by suction in order to eliminate its action.

The need for a method of measuring carpet wear is evident. Change in appearance does not lend itself to quantitative expression. Carpets change in weight and in thickness of pile when they wear. Both of these changes were studied. Change in thickness appears to be the most useful measure of wear for laboratory tests. A sensitive thickness gage was devised for use with the machine, and is described in the paper.

## II. THE MACHINE

### 1. DESCRIPTION

Figure 1 is a photograph of the carpet wear testing machine. The carpet to be tested is tacked on a wood-covered metal disk or turntable 17 inches in diameter. The turntable is placed over the end of

[1] This machine is similar in principle to one developed for the testing of sole leather. See Hart and Bowker, An Apparatus for Measuring the Relative Wear of Sole Leathers, and the Results Obtained With Leather From Different Parts of a Hide. B. S. Tech. Paper No. 147; 1919.

a vertical shaft which is mounted in a special bearing at one end of a lever so that when a weight is hung at the other end of the lever the carpet is brought to bear with equal vertical force against each of two leather-faced[2] pulleys. The lever arms are approximately balanced, and the leverage ratio is 6 so that the vertical force against each pulley is three times the applied weight.

The pulleys are 15 inches in diameter and 2 inches wide. They are spaced 11 inches from center to center and located equidistant from the center of the turntable. The driving pulley, at the left in the photograph, is rotated by a motor through a suitable speed reducer. The speed of this pulley may be varied by changing the speed of the motor. The free pulley, at the right in the photograph is free to rotate on the shaft of the driving pulley. A brake drum, 12 inches in diameter and 2 inches wide, is fastened to the free pulley. A leather brake belt passing over this drum has one end fastened to a spring balance while a weight is suspended on the other end. The braking torque, which is the difference between the weight and the reading of the spring balance multiplied by the radius of the brake drum may be varied by changing the weight.

## 2. THEORY

When the machine is in operation the driving pulley, which is rotated by the motor, causes the turntable to rotate and this in turn drives the free pulley. By a suitable combination of speed of turntable, vertical force against each pulley, and braking torque on the free pulley the forces on the pile of the carpet, which is mounted on the turntable, may be controlled. The pulleys will exert a given downward force on the carpet which is determined by the weight on the lever. The frictional force between the driving pulley and the carpet depends upon the coefficient of friction and the normal force, and is great compared to the resisting force produced by friction in the bearings. Consequently, there will be no appreciable slipping of the driving pulley on the carpet when the brake is unloaded. To produce slipping a definite resisting torque is applied by means of the brake. A slight twisting action is produced on the pile of the carpet because of the fact that the carpet is rotating in a plane perpendicular to the plane of rotation of the pulleys. The forces acting on the carpet are, therefore, a vertical force, a horizontal force acting in one direction at one pulley and in the opposite direction at the other, and a rotary motion, all accompanied by slipping. Thus the bending, twisting, slipping, and compression of the pile which takes place when carpets are walked upon is simulated.

The vacuum cleaner shown in Figure 1 is run continuously during the test. It removes the abraded material which has been found to affect the result if allowed to accumulate. It also serves to keep the carpet approximately at room temperature by drawing a considerable volume of air over it. The inlet just touches the pile of the carpet at the beginning of the test.

## 3. TEST PROCEDURE

Circular samples 15 inches in diameter are cut from the carpet to be tested. These samples are conditioned at a temperature of 70° F.

[2] The leather used on the pulleys is 2-inch belting conforming to the requirements of U. S. Government standard specification No. 37, Circular of the Bureau of Standards No. 148.

and relative humidity of 65 per cent for at least four hours before the test. A specimen is tacked on the turntable which is then put in place on the machine. The weight at the end of the lever is made equal to one-third of the desired downward force on the carpet in contact with each pulley. Because of the difference in the diameters of the brake drum and the free pulley the effective load on the brake is one and one-fourth times the desired horizontal force on the pile of the carpet. The number of revolutions made by the turntable is obtained by means of a revolution counter.

Two methods were employed to measure the rate of wear on the carpet. The first method consists in collecting the material worn off, which is conditioned and weighed. The weight of material removed

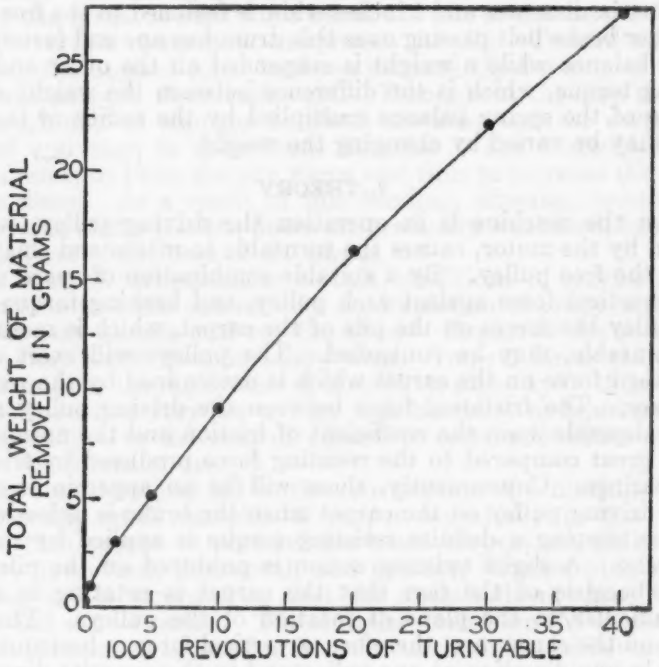


FIGURE 2.—*Results of a test showing the total weight of material removed*

plotted against the total number of revolutions of the turntable gives one measure of the rate of wear on the carpet. The material removed is very light and must be weighed on an analytical balance. Furthermore, it must be collected in a rather large bag which is attached to the vacuum cleaner. Because of the bulky bag the weighing is awkward and the consistency of results depends to a great extent upon thorough conditioning. Although a plot showing the weight of material removed against number of revolutions of the turntable (fig. 2) gives an indication of the rate of wear of the carpet, it does not show when the pile of the carpet is completely worn off, because the base of the carpet starts to wear when the pile is badly worn. The weighing of the abraded material does not appear to be as satisfactory a method of judging the wear as the second method tried.

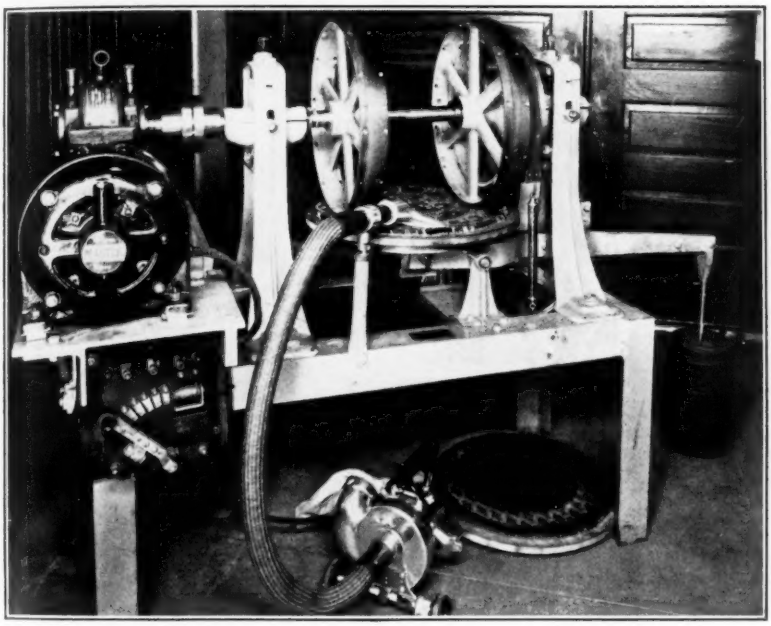

FIGURE 1.—*Carpet wear testing machine*

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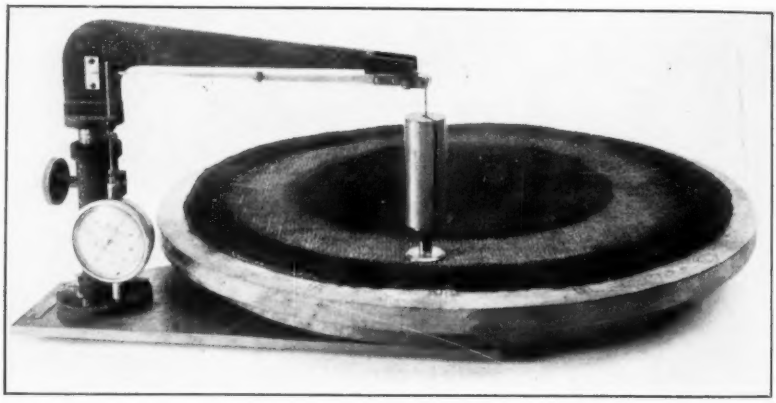

FIGURE 3.—*Gage for measuring thickness of carpet*

The second method consists in measuring the thickness of the carpet at regular intervals with a special thickness gage which is shown in Figure 3. A cylindrical foot 1 inch in diameter and carrying a net weight of 0.59 pound, which is eqivalent to 0.75 lb./in.$^2$, rests on the pile. This compresses the pile an amount which depends upon the density of pile and upon the stiffness of the pile fibers. The resistance to compression due to stiffness of the pile fibers may be considerable before wear, but after a few revolutions of the turntable under the desired downward force it becomes negligible. Therefore thickness measurements taken after a few revolutions give an accurate indication of the amount of pile in the carpet or pile density. It also gives a definite indication when all of the pile is worn off, namely, when the thickness of the carpet is equal to the thickness of the base where all of the pile has been pulled out. The decrease in carpet thickness gives an indication of the apparent initial wear and of the wear of the carpet. Thickness measurements were taken before wear and after a given number of revolutions of the turntable at 8 points, spaced 45° apart on the worn portion of the carpet. The average of these 8 measurements is the thickness of the carpet referred to in Figures 4 to 8, inclusive.

Some carpets wear more rapidly where the pile fibers are bent across the shots than where they are bent parallel to the shots. For this reason it is not considered satisfactory to test more than one specimen at a time which otherwise could be done by tacking sectors of different carpets on the turntable. Carpets which wear unevenly should have thickness measurements made at 16 points, spaced 22.5° apart on the worn portion of the carpet, instead of at only 8 points.

## III. PERFORMANCE TESTS

In order to bring out the characteristics of the carpet wear testing machine, a series of tests were made on specimens taken from the same velvet carpet. An analysis of this carpet gave the following results:

| | | | | |
|---|---|---|---|---|
| Wires per inch | | 9 | | |
| Binders per inch | | 16 | | |
| Stuffers per inch | | 32 | | |
| | | | Per cent | |
| Weight of carpet | oz./yd.$^2$ | 53 | or | 100 |
| Weight of pile | do | 20.1 | or | 38 |
| Weight of stuffers | do | 16.5 | or | 31 |
| Weight of binders | do | 6.4 | or | 12 |
| Weight of shots | do | 10.0 | or | 19 |

Pile is all wool.

### 1. DUPLICATION OF RESULTS

Three specimens from the same carpet were tested, using a downward force of 150 pounds on the carpet at each pulley, a brake load of 15 pounds, and a turntable speed of 80 r. p. m. The results are shown graphically in Figure 4, where the open circles, solid circles, and solid squares denote the results for the three specimens, respectively. The broken horizontal line represents the thickness of the base of the carpet where all of the pile has been pulled out.

The results for the three tests are in good agreement. A mean curve is drawn through these points which is used for comparison with tests made under different test conditions.

### 2. DOWNWARD FORCE ON CARPET

In Figure 5 the curve through the solid circles is the mean curve of Figure 4. The curves through the solid triangles and solid squares represent the results for tests in which the downward force at each pulley was changed from 150 to 75 and 202.5 pounds, respectively, while the brake load and speed of turntable were kept constant at 15 pounds and 80 r. p. m., respectively. These curves show that the rate of wear of the carpet increases rapidly with the downward force.

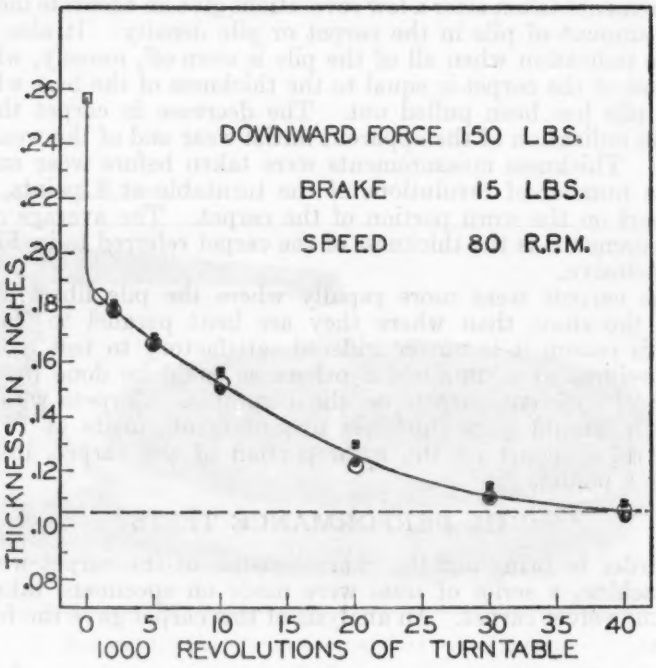


FIGURE 4.—*Results of three tests of same carpet*

### 3. BRAKE LOAD

In Figure 6 the curve through the solid circles is the mean curve of Figure 4. The curves through the solid triangles and solid squares represent the results for tests in which the brake load was changed from 15 to 0 and 25 pounds, respectively, while the downward force and speed of turntable were kept constant at 150 pounds and 80 r. p. m., respectively. These curves show that the rate of wear of the carpet increases slightly with the brake load.

### 4. SPEED OF TURNTABLE

In Figure 7 the curve through the solid circles is the mean curve of Figure 4. The curves through the open circles, solid triangles, and solid squares represent the results for tests in which the speed of the turntable was changed from 80 to 30, 60, and 100 r. p. m., respectively, while the downward force and brake load were kept constant at 150 and 15 pounds, respectively. It will be noted that

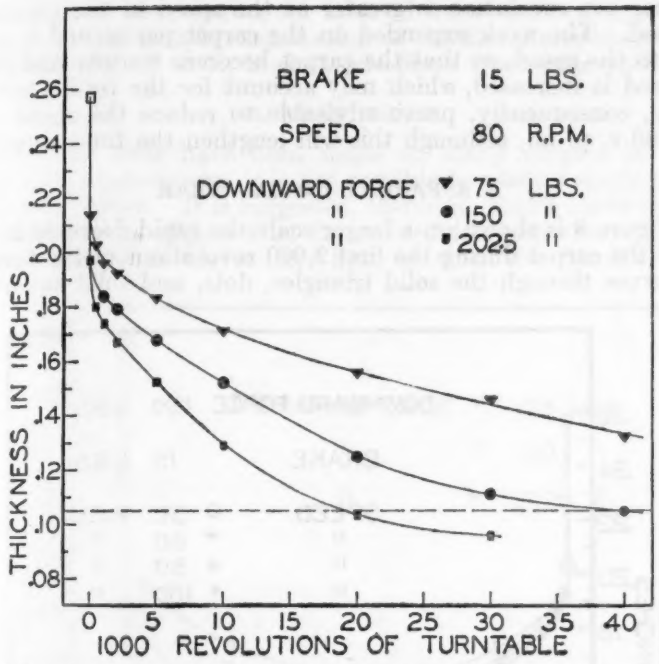


FIGURE 5.—*Results of three tests showing the effect of downward force on the wear of the carpet*

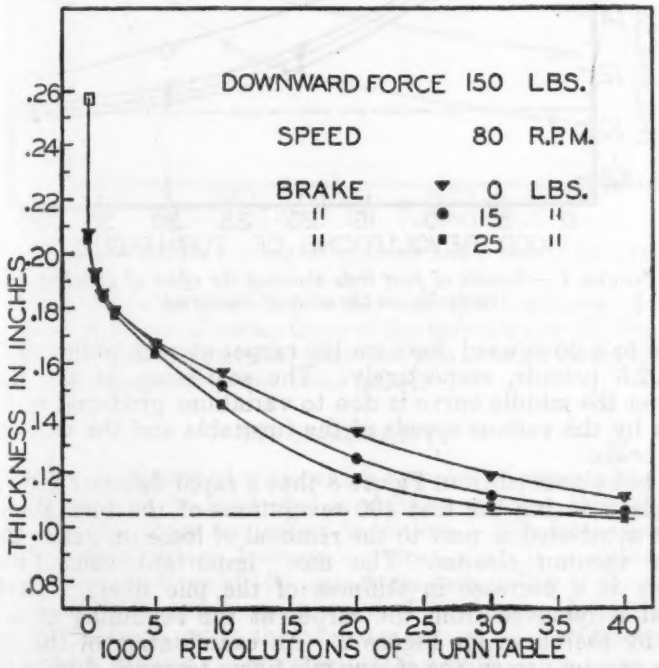


FIGURE 6.—*Results of three tests showing the effect of brake load or slipping on the wear of the carpet*

the wear per revolution is greater as the speed of the turntable is increased. The work expended on the carpet per second is proportional to the speed, so that the carpet becomes warmer and drier as the speed is increased, which may account for the results obtained. It may, consequently, prove advisable to reduce the speed of test below 80 r. p. m., although this will lengthen the time required for a test.

### 5. APPARENT INITIAL WEAR

In Figure 8 is shown on a larger scale the rapid decrease in thickness of the carpet during the first 2,000 revolutions of the turntable. The curves through the solid triangles, dots, and solid squares cor-

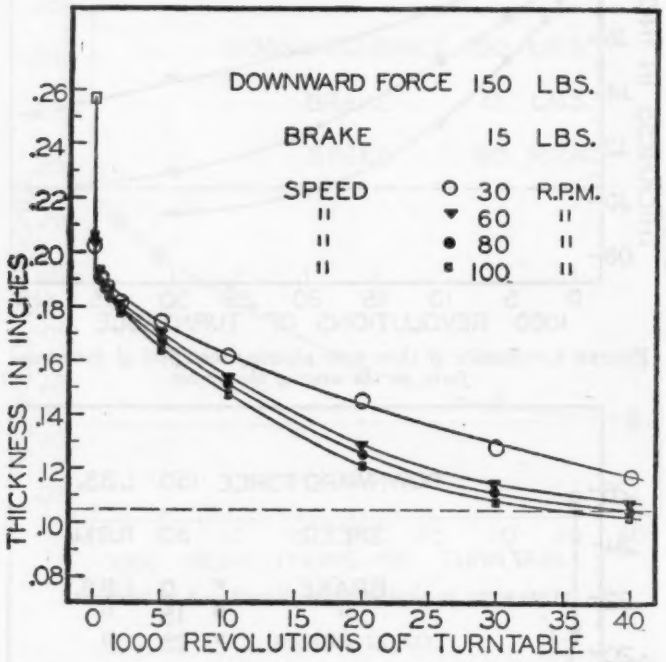


FIGURE 7.—*Results of four tests showing the effect of speed of the turntable on the wear of the carpet*

respond to a downward force on the carpet at each pulley of 75,150, and 202.5 pounds, respectively. The scattering of the observed points on the middle curve is due to variations produced in the rate of wear by the various speeds of the turntable and the various loads on the brake.

It is to be noticed from Figure 8 that a rapid decrease in thickness takes place during the first 100 revolutions of the turntable. This may be attributed in part to the removal of loose or weak pile fibers by the vacuum cleaner. The mos important cause, however, probably is a decrease in stiffness of the pile fibers. That more material is removed from the carpet at the beginning of a test is shown by the curve for Figure 2. An examination of the material shows a greater percentage of long pile fibers removed during the first

500 revolutions than during the interval from 30,000 to 40,000 revolutions. A microscopic examination of the fine material shows that it is practically all wool; that is, pile fibers worn into small shreds.

### 6. WEAR INDEX

Until wear tests have been made on many carpets of varying grades and constructions, it is not possible to select a single quantity as the wear index. It is suggested, therefore, that a curve similar to the one shown in Figure 4 be determined for each test. If after a sufficient number of curves have been obtained it is found that none

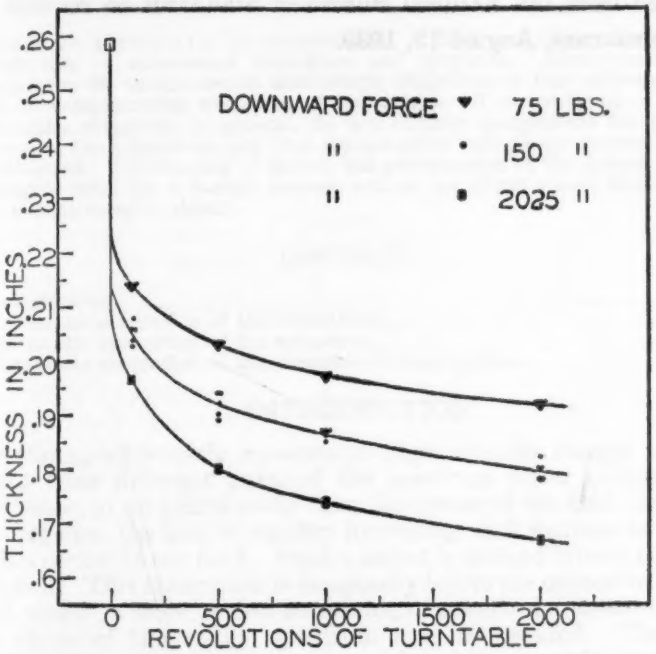


FIGURE 8.—*Results showing the apparent initial wear of the carpet*

of these curves intersect, then either (*a*) the thickness of the pile after a given number of revolutions of the turntable or (*b*) the number of revolutions of the turntable after the pile is worn down to a given thickness may be used as the wear index.

## IV. SUMMARY

A machine is described with which samples of carpets and similar floor coverings can be subjected to definite wearing forces that can be varied at will under controlled conditions. The forces are chosen to resemble those which bear on a carpet when it is walked upon. Using a downward force of 150 pounds on each pulley of the machine, a brake load of 15 pounds and a speed of 80 r. p. m. of the turntable, carpets can be worn out in the course of one day. Performance tests show that the machine gives reproducible results.

The decrease in thickness of the pile of the carpet during the test is found to be a more convenient criterion of wear than decrease in weight. A thickness gage for use with the machine is described.

The machine can be used to test the relative durability of carpets under definitely specified conditions. Whether the results are a satisfactory measure of probable relative durability of carpets in service has not been determined.

The machine should be useful for studies of the effect of various factors on carpet wear and for studies of the relation between composition and construction of carpets and their resistance to wear.

Working drawings for the construction of the machine may be obtained from the National Bureau of Standards on request.

WASHINGTON, August 12, 1930.

# THE LATERAL CHROMATIC ABERRATION OF APOCHROMATIC MICROSCOPE SYSTEMS

By I. C. Gardner and F. A. Case

ABSTRACT

Methods are described for the measurement of the lateral chromatic aberration and distortion of microscope objectives and eyepieces. Measurements have been made on 20 apochromatic microscope objectives of four different makes, and on 10 compensating eyepieces of two makes. The results show that the compensating eyepieces, in general, do not entirely compensate the chromatic aberration of the objectives, and that the complete microscope system is usually undercorrected. The bearing of this on the performance of the system in photomicrographic work by a 3-color process and in the direct visual observation of objects is considered in detail.

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## I. INTRODUCTION

For the apochromatic microscope objective the images produced by light from different parts of the spectrum differ in size. As a consequence, at all points other than the center of the field, the images do not register, the lack of registry increasing with increase of distance from the center of the field. Such a defect is termed lateral chromatic aberration. This aberration is designedly left in the objective because, by this means, a more perfect correction of spherical aberration for the entire range of the visible spectrum may be secured. The lateral chromatic aberration in the image, produced by the objective, is then compensated by the eyepiece which introduces a lateral chromatic aberration of the opposite sense, thus giving origin to the designation "compensating eyepiece." For the objectives of shorter focal length and greater numerical aperture the limitations of the optical materials available prescribe the amount of lateral chromatic aberration present. For the objectives of longer focal length and smaller aperture ratio, the lateral chromatic aberration, although it could be more perfectly corrected without detriment to the correction for spherical aberration, is made the same in amount as that for the objectives of greater numerical aperture in order that all of a series may be used interchangeably with a single series of compensating eyepieces.

For very precise work it may then become a question whether or not the lateral chromatic aberration is held sufficiently constant for the different focal lengths to give the desired freedom from color and also whether or not the lateral chromatic aberrations of objective

and eyepiece are sufficiently standardized to permit the interchangeable use of an objective of one manufacturer with an eyepiece manufactured by another. The present investigation is the result of a question of this character which arose in connection with the making of photomicrographs for 3-color reproduction at the U. S. Army Medical Museum. In such work three photographs are taken successively through Eastman photographic filters, A, B, and C, which correspond approximately to wave lengths 620, 550, and 450 mμ, respectively, and from these three photographs the three plates are made for producing the impressions in three different colors which form the final color print. Such work constitutes a more severe test of the color correction of a system than does the more conventional use of the microscope, since a very slight lack of register in the color print may be detected and is considered objectionable.

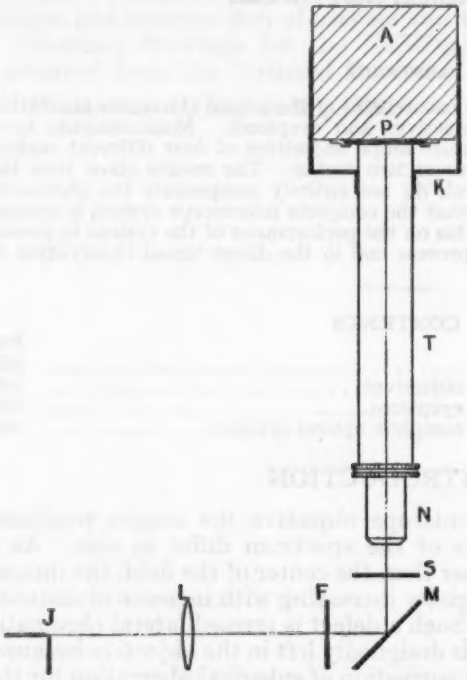


FIGURE 1.—*Arrangement for testing the objectives*

It should be mentioned that this use does not strictly accord with the conditions for which the microscope system is designed. When the microscope is used for the direct visual examination of an object, the image formed by the eyepiece is virtual, whereas when used for photographic purposes the image is real. The difference arising from this variation in use is probably not important because in both cases the image distance is large in comparison with the focal length of the eyepiece.

## II. CHROMATIC ABERRATION OF THE OBJECTIVES

The method of test applied to the objective is illustrated in Figure 1. A microscope stand (not indicated in the figure) was adjusted to bring the tube *T* in a vertical position and the objective to be tested was mounted in the usual position at *N*. On the stage of the microscope was placed the object *S*, which was a glass slide carrying a series of parallel lines, spaced 0.1 mm ruled in silver by means of a diamond point. The arc at *J*, the condenser lens *L*, and the mirror *M*, with the Eastman A, B, and C filters, which were mounted in turn at *F*, formed the illuminating system. The photographic plate *P*, approximately 25 mm square, rested on the upper end of the draw tube which was adjusted to bring the plate in the image plane cor-

responding to a tube length of 160 mm. Stray light from the room was excluded by the brass cup $K$, mounted on the upper end of the microscope tube, and by the wooden plug $A$, to which the plate was loosely attached in order to facilitate its removal from the brass cup after the exposure.

For each objective three negatives were obtained, one corresponding to each of the three filters. The spacing of the lines in the image, as recorded on the negative, was measured on a comparator and the magnification obtained by dividing the distance between two lines on the negative by the distance between the two homologous lines on the object slide. This comparison of distances was made for each pair of adjacent lines recorded on the plate. If there were an appreciable amount of distortion the values of the magnification thus obtained for any one lens would have changed systematically, either increasing or decreasing, as pairs of lines were selected farther from the center of the field. In none of the objectives tested was such a progressive change found, and it is concluded that the distortion present is substantially less than that corresponding to a variation in magnification of 0.1 per cent for the different parts of a field 18 mm in diameter.

Table 1 gives the results of measurements which have been made on 20 objectives of four different makes.

TABLE 1.—*Magnification ratios of objectives tested*

| Reference No. | Make | Focal length (mm) | Magnification, B filter | Magnification, B filter divided by magnification, A filter | Magnification, C filter divided by magnification, A filter |
|---|---|---|---|---|---|
| 1 | I | 4 | 33.9 | 1.005 | 1.014 |
| 2 | I | 8 | 16.4 | 1.005 | 1.014 |
| 3 | I | 8 | 16.6 | 1.005 | 1.012 |
| 4 | I | 16 | 8.2 | 1.005 | 1.014 |
| 5 | I | 16 | 7.8 | 1.006 | 1.015 |
| 6 | I | Average | | 1.005 | 1.014 |
| 7 | II | 4 | 39.2 | 1.006 | 1.015 |
| 8 | II | 4 | 37.0 | 1.005 | 1.016 |
| 9 | II | 8 | 16.5 | 1.006 | 1.017 |
| 10 | II | 8 | 16.8 | 1.005 | 1.016 |
| 11 | II | 16 | 8.3 | 1.004 | 1.013 |
| 12 | II | 16 | 8.2 | 1.006 | 1.014 |
| 13 | II | 16 | 8.1 | 1.005 | 1.013 |
| 14 | II | Average | | 1.005 | 1.015 |
| 15 | III | 3 | 45.5 | 1.003 | 1.017 |
| 16 | III | 4 | 35.9 | 1.007 | 1.019 |
| 17 | III | 8 | 17.4 | 1.004 | 1.012 |
| 18 | III | 16 | 8.1 | 1.006 | 1.020 |
| 19 | III | 16 | 9.0 | 1.006 | 1.018 |
| 20 | III | Average | | 1.005 | 1.017 |
| 21 | IV | 2 | 57.7 | 1.000 | 1.007 |
| 22 | IV | 4 | 36.0 | 1.005 | 1.013 |
| 23 | IV | 16 | 8.7 | 1.005 | 1.013 |
| 24 | IV | Average | | 1.003 | 1.011 |

The fourth column gives the magnification for the B filter, the fifth the ratio of magnification for B filter to the magnification for A filter, and the sixth column the ratio of magnification for C filter to magnification for A filter. If there were no primary lateral chromatic

aberration the A and C images would be of the same size and the ratios in the sixth column would be 1. Reference to these ratios shows that the A image is smaller than the B image which, in turn, is smaller than the C image. The image of a white point source not on the axis of the objective will, therefore, be a short spectrum, placed radially in the field with the red end turned toward the center. If one of these apochromatic objectives were used to produce an image 250 mm in diameter with no compensation introduced by the eyepiece, then for the A and C images of a point at the edge of the picture the failure to register would be of the order of 2 mm. This illustrates the importance of compensation and indicates why the prominent colored fringes are observed when the apochromat is used with an eyepiece which is not compensating. Reference to the average values for the different makes shows that III and IV differ most in the character of compensation which their objectives offer. Again, using a projected image 250 mm in diameter as an illustration, an eyepiece which compensated an objective of Group III perfectly, might, if used with an objective of Group IV, give A and C images which fail to register at the edge of the picture by 0.8 mm.

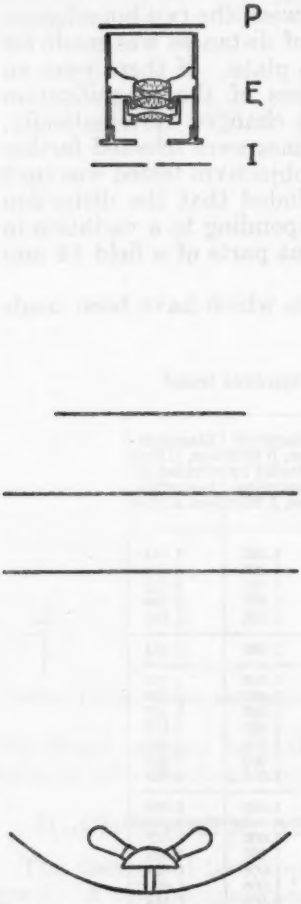


FIGURE 2.—*Arrangement for testing the eyepieces*

## III. CHROMATIC ABERRATION OF THE EYEPIECES

The arrangement for testing an eyepiece is shown in Figure 2. The source of light was a diffusing screen of opal glass at *B*, illuminated by a cluster of incandescent lamps near the focus of a concave reflector, *R*, built up from small pieces of plane mirrors mounted in a frame. This illuminating system is of the type commonly marketed by photographic supply houses for illuminating negatives which are to be enlarged without the use of a condensing lens. The object at *Q* was a 10-inch strip of glass coated with silver bearing ruled parallel lines spaced 4 mm. The filters were of gelatine, 8 by 10 inches, mounted loosely between two sheets of glass and placed at *F* between the object and the diffusing screen of the illuminating system. The eyepiece to be tested was at *E* with the eye end toward *Q*.

All of the eyepieces were positive, a characteristic which is essential for this method of test. The optical system of each eyepiece was

removed as a unit and mounted in a shorter tube in order that a small photographic plate might be conveniently placed in the image plane. The diaphragm at $I$ was 0.8 mm in diameter and was placed, with reference to the eyepiece, in the plane occupied by the exit pupil of the eyepiece when it is mounted in a microscope. The use of this diaphragm is quite necessary, as otherwise a much larger beam of light would be transmitted by the eyepiece in this testing apparatus than in normal use, the position of the pupil points would be quite different, and the distortion and lateral chromatic aberration would be greatly changed. The image is received on the photographic plate at $P$. The distance from the eyelens to the object $Q$ was 26 cm and the half angle of the field of view on the eye side of the eyepiece was approximately 17°. With the arrangement of parts as indicated it will be recognized that the course of the rays corresponds to that when the eyepiece is used for projection purposes with the screen distant 26 cm, except that the course of the rays is reversed and object and image are interchanged. This arrangement involving a reversal in the direction of travel of the light was adopted because it was more convenient to measure the small negatives thus secured. As in the case of the objectives, filters $A$, $B$, and $C$ were used, and

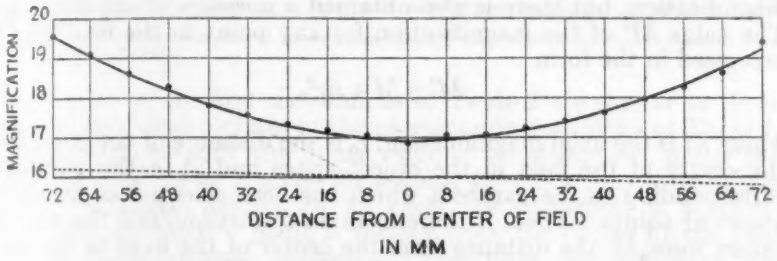


FIGURE 3.—*Variation of magnifications with distance from the center of the field for a typical eyepiece*

the magnification determined by comparing the distances between homologous pairs of adjacent lines on the object and negative. The values referred to as magnifications will be the ratios of lengths at Q to lengths at $P$, thus corresponding to the magnification when light traverses the eyepiece in the usual direction. In subsequent references the terms, object and image, will refer to the planes at $P$ and Q, respectively; that is, they refer to object and image as the eyepiece is commonly used and not to the condition of this test in which the direction of travel of the light is reversed.

For the objectives the magnification obtained for pairs of lines at different distances from the center of the field showed no systematic variation, but, in contrast with this, for the eyepieces the magnification increases as the place of measurement recedes from the center of the field, thus indicating the presence of a considerable amount of positive distortion. Figure 3 illustrates a typical set of observations in which the value of the magnification as observed is 16.90 at the center of the field and 19.60 at the edge. If it be assumed that only distortion of the third order is present, the change in magnification will vary as the square of the distance from the center of the field, and the points located in Figure 3 should lie on a parabola. Accord-

ingly, for each set of observations, such as is shown in Figure 3 (except as noted below), a parabola has been drawn which fits the observed points satisfactorily and the ordinate of the vertex of this parabola has been taken as the value of the axial magnification. The choice of parabolas was determined by first drawing a family of parabolas of different curvatures on transparent paper and superposing the parabolas in turn upon the plotted observations.[1] Two eyepieces were found which gave curves to which parabolas could not be fitted satisfactorily. One showed such excessive distortion that it is believed to have been incorrectly assembled or otherwise defective. The other showed an unusually small amount of distortion, the third and higher orders compensating each other at a point near the edge of the field. For all the other eyepieces tested the observed points could be fitted very closely by a parabola. In such cases, it is evident that the ordinate at the vertex of the parabola gives a better value of the axial magnification than if the measured value at the center of the field were taken because the measurement to the vertex of the parabola gives weight to all the observed points.

After the parabola which satisfactorily fits the observations has been selected, one has not only determined a value of the axial magnification, but there is also obtained a measure of the distortion. The value $M'$ of the magnification for any point in the field may be expressed in the form

$$M' = M + Ar^2_0 \tag{1}$$

where $M$ is the axial magnification, $r_0$ is the distance of the point from the center of the field in the object space and $A$ is the parameter corresponding to the parabola which has been selected as fitting the observed points. Then, if there were no distortion, and the magnification were $M$, the distance from the center of the field to the point in the image conjugate to $r_0$ would be $Mr_0$. With distortion present, this distance is

$$\int_0^{r_0} (M + Ar^2)dr = Mr_0 + \frac{1}{3}Ar^3_0 \tag{2}$$

and the linear distortion; that is, the displacement arising from the distortion, measured in the image plane, is

$$\frac{1}{3}Ar^3_0 = \frac{1}{3}\frac{Ar^2_0}{M}Mr_0 \tag{3}$$

for the point $r_0$. If $r_0$ denotes a point at the extreme edge of the field, $Mr_0$ is the diameter of field in the image plane when the aberrations are neglected and $Ar^2_0$ is the difference in the ordinates, at center and edge of field, for the parabola which has been drawn to fit the observed points.

Table 2 gives the results of tests on 10 eyepieces of two different makes.

[1] The dotted line is perpendicular to the axis of the parabola. It is oblique with respect to the coordinate axes because of a slight lack of parallelism of object and photographic plate. The effect of such tilts was considered when measuring the distortions.

TABLE 2.—*Axial magnification ratios and distortion constants of eyepieces tested*

| Reference No. | Make | Nominal magnification | Magnification B filter | Magnification B filter divided by magnification A filter | Magnification C filter divided by magnification A filter | Linear distortion, 12° from axis | Angular distortion 12° from axis | Excess of angular distortion for C image over that for A image, 12° from axis |
|---|---|---|---|---|---|---|---|---|
| | | | | | | *mm* | *Minutes* | *Minutes* |
| 1 | I | 20 | 20.4 | 0.996 | 0.990 | 0.87 | 11.0 | −1.5 |
| 2 | I | 15 | 15.3 | 1.003 | .999 | .44 | 5.6 | −1.8 |
| 3 | I | 15 | 15.2 | .997 | .988 | .73 | 9.3 | −3.5 |
| 4 | I | | 16.9 | .998 | 1.000 | 1.32 | 16.8 | −3.4 |
| 5 | I | | 12.1 | .997 | .980 | | | |
| 6 | I | Average | | .998 | .991 | .84 | 10.6 | −2.6 |
| 7 | II | 25 | 25.9 | .995 | .985 | 1.03 | 13.1 | −2.0 |
| 8 | II | 25 | 25.2 | .997 | .986 | 1.06 | 13.5 | −2.0 |
| 9 | II | 25 | 25.4 | .998 | .984 | .79 | 10.0 | −.9 |
| 10 | II | 15 | 15.5 | 1.000 | .982 | 1.00 | 12.7 | −1.6 |
| 11 | II | 15 | 14.9 | 1.000 | .995 | | | |
| 12 | II | Average | | .998 | .996 | .97 | 12.3 | −1.6 |

NOTE.—For eyepiece No. 5 the third and higher order aberrations were so well balanced that the magnification at the edge of field was substantially the same as at the axis. It would, therefore, be misleading to give a measure of distortion based on third order analysis. For practical purposes it may be considered to be distortion free.

For eyepiece No. 11 the aberration of orders higher than third are so great that values based on third order analysis are not given.

The values in the first six columns of Table 2 are similar to those tabulated for the objectives in the corresponding columns of Table 1. In the seventh column, the linear value of the distortion, under the conditions of the test, is given for a point 12° from the center of the field in the image space. In all cases the distortion is positive; that is, the image of a point is farther from the center of the field than its distortion-free position. These data for distortion are based upon measurements of the B image. For all eyepieces tested, the distortion for the C image is the same as for the B image, and the distortion for the A image is greater than for the B or C images. This excess of distortion for the A image over that for the B or C image is a chromatic difference in distortion which modifies the lateral chromatic aberration, its importance increasing as points farther from the center of the field are considered. The values tabulated in column 9 are for a point 12° from the center of the field and, therefore, correspond directly with the values of column 7. It may at first seem questionable to obtain, as has been done in Table 2, an average value for the distortion of the eyepiece of a given make by the process of averaging distortion constants for eyepieces differing in focal length. When, however, it is remembered that these eyepieces are designed to be used interchangeably with different objectives, it becomes apparent that this procedure is legitimate.

In the eighth column of Table 2, the angular values of the distortion for the B image at a point 12° from the center of the field are tabulated. Although these values are derived from measurements corresponding to a real image 260 mm. from the exit pupil, the angular value of the distortion remains approximately constant for any object distance, and this value, therefore, affords a means for determining the linear distortion for object distances differing from those of this test.

## IV. CHROMATIC ABERRATION OF THE COMPLETE OPTICAL SYSTEM

The product of the magnification of the objective by the magnification of the eyepiece gives the total magnification for the optical system and similarly the product of the two magnification ratios gives the corresponding magnification ratio for the complete system. If the ratio magnification, filter C, divided by magnification, filter A, is 1, and if there is no chromatic variation in distortion, the A and C images will be of the same size, the registry of the two images will be perfect at all points of the field and there will be no primary lateral chromatic aberration for the effective wave lengths of filters A and C. If this condition is not realized the departure of this ratio from 1, multiplied by the radius of the field in the image space, expressed in either linear or angular units, will give, in the corresponding units, the distance between the A and C images of a point at the edge of the field when the chromatic variation in distortion is ignored. These values for a point 12° from the center of the field are tabulated in Table 3, column 7. Column 8 gives for the same point, the relative displacement of the A and C images which arises from the chromatic variation in distortion of the eyepiece. These latter values are taken directly from Table 2, column 9. By adding these two displacements for each combination, the angualr values of the lateral chromatic aberration for the complete system are obtained. Table 3 gives results of this character for several different combinations of the objectives and eyepieces which have been tested.

TABLE 3.—*Axial magnification ratios and lateral chromatic aberration of selected combinations of objectives and eyepieces*

| Reference No. of combination | No. of objective (see Table 1) | Make | No. of eyepiece (see Table 2) | Make | Magnification, C filter divided by magnification, A filter, for complete system | Angular lateral chromatic aberration arising from difference in magnification | Angular chromatic difference in distortion | Lateral angular chromatic aberration at point 12° from center of field |
|---|---|---|---|---|---|---|---|---|
| | | | | | | *Minutes* | *Minutes* | *Minutes* |
| 1 | 6 | I | 6 | I | 1.005 | +3.6 | −2.6 | +1.0 |
| 2 | 14 | II | 6 | I | 1.006 | +4.3 | −2.6 | +1.7 |
| 3 | 20 | III | 6 | I | 1.008 | +5.8 | −2.6 | +3.2 |
| 4 | 24 | IV | 6 | I | 1.002 | +1.4 | −2.6 | −1.2 |
| 5 | 6 | I | 12 | II | 1.000 | 0.0 | −1.6 | −1.6 |
| 6 | 14 | II | 12 | II | 1.001 | + .7 | −1.6 | − .9 |
| 7 | 20 | III | 12 | II | 1.003 | +2.2 | −1.6 | + .6 |
| 8 | 24 | IV | 12 | II | .997 | −2.2 | −1.6 | −3.8 |
| 9 | 6 | I | 2 | I | 1.013 | +9.4 | −1.8 | +7.6 |
| 10 | 6 | I | 5 | I | .994 | −4.3 | 0 | −4.3 |
| 11 | 6 | I | 7 | II | .999 | −.7 | −2.0 | −2.7 |
| 12 | 6 | I | 10 | II | .996 | −2.9 | −1.6 | −4.5 |

Reference to Tables 1 and 2 indicates that the variation in the magnification ratios is greater for the eyepieces than for the objectives. The first four combinations listed in Table 3 show the effect of combining an average objective of each make listed in Table 1 with the average eyepiece of the make designated I in Table 2. The angular values of the lateral chromatic aberration resulting from the

combined effects of the chromatic differences in magnification and distortion are tabulated in the last column of Table 3. These values vary from −1.2 to +3.2 minutes. The tabulated values are for a point 12° from the axis in a real image plane distant 260 mm from the exit pupil and a positive value indicates that the image of a point formed by light transmitted by the blue (C) filter lies farther from the center of the field than does the corresponding image formed by light transmitted by the red (A) filter.

Similarly combinations Nos. 5 to 8, inclusive, embody the results obtained when the average objective of each make listed in Table 1 is combined in turn with the average eyepiece of the make designated II in Table 2. For these combinations the average lateral chromatic aberration varies from −3.8 to +0.6 minutes. Combinations Nos. 9 to 12, inclusive, are obtained by combining the average objective of make I listed in Table 1 with individual eyepieces of which each was selected because in one or more features it manifests an extreme variation from the normal characteristics of the group.

The results in the final column of Table 3 are expressed in angular units and they may, therefore, be expected to give a good approximation to the lateral chromatic aberration present, either when the image is real and projected as in photomicrography or when the image is virtual as when a microscope is used for the visual examination of an object. The significance of the results, however, are somewhat different for these two cases and it is advantageous to consider them separately.

The photographic application will be considered first. If the film which receives the image is 260 mm from the exit pupil, as in the present test, one minute of arc corresponds to approximately 0.1 mm linear displacement in the plane of the screen. With this projection distance, therefore, if one of the optical combinations considered above is used to make color separation negatives for producing photo-engraved plates from which the red, yellow, and blue impressions which form a color print are made, it follows that the impressions made by the three plates at a point 55 mm (12°) from the center of the field will fail to register by from 0.1 to 0.8 mm. accordingly as the different systems listed in Table 3 are employed. This lack of registry is much more harmful in the color print than in a virtual image. In the color print there are three images in contrasting colors and they differ in size by finite amounts, whereas, in the virtual image, if the illumination is by white light, there is an infinity of images varying in a continuous manner in size and color. Furthermore the virtual image, under all conditions of viewing, has approximately the same angular dimensions, whereas, the color print is apt to be brought close to the observer's eye for careful scrutiny with consequent angular enlargement. These considerations indicate that much greater freedom from lateral chromatic aberration is necessary for 3-color photomicrography than for the usual use of a microscope.

The eyepieces of this test are not of the type specially designed for photomicrographic work and the results obtained indicate that one can not expect satisfactory results from the commercial product except when the eyepiece and objective are specially selected for that purpose. Special types of eyepieces are made for projection purposes. They should not only be expected to give a better performance as

regards freedom from chromatic aberration, but should also be mor nearly free from distortion. This test shows that considerable dis tortion is present in the ordinary compensating eyepiece and this i probably made necessary by the condition that the eye distance b relatively large, a requirement which need not be imposed on th projection eyepiece.

If the eyepieces are to be used in the usual manner for visual ob servations the angular values of the lateral chromatic aberrations whic are tabulated in the final column of Table 3 need not be converted int linear units. In view of the fact that the angular limit of resolution for the eye is one minute one would expect the systems with larg amounts of chromatic aberration to show excessive color fringes.

The prominence of these color fringes, however, may be very muc lessened by the compensating chromatic aberration which results fro an eccentric placement of the entrance pupil of the observer's eye wit respect to the exit pupil of the microscope. Conrady [2] has called at tention to this chromatic aberration of the eye which is unconsciously introduced by the observer in order to improve the definition of th image. If the eccentricity between the pupil of the eye and tha of the microscope is 1 mm there are introduced approximately thre minutes of compensating chromatic aberration which is negativ and therefore tends to correct an undercorrected system. Referenc to Table 3 indicates that under suitable conditions it is possible t correct a large portion of the chromatic aberration of any of the under corrected systems in this manner although it should not be understood that this method of compensation makes a fairly complete eliminatio of chromatic aberration in the microscope unneccessary. It rathe signifies that such chromatic aberration as remains in the microscop system should be positive rather than negative. Reference t Table 2 indicates that the average values of the magnification con stants for eyepieces of makes I and II correspond closely to th desired values as indicated by the magnification constants of th objectives of corresponding makes listed in Table 1, although in eac case individual eyepieces show rather large discrepancies. Further more, for these two makes greater uniformity is shown by the objec tives than by the eyepieces.

WASHINGTON, March 18, 1931.

[2] Applied Optics and Optical Design, 1, p. 510. Published by Oxford University Press; London.

# PHASE EQUILIBRIA IN THE SYSTEM $Cr_2O_3$-$Al_2O_3$

By E. N. Bunting

ABSTRACT

A study of the phase equilibria in the $Cr_2O_3$-$Al_2O_3$ system has shown these ides to be completely miscible in the liquid and solid states, with no compound rmation. The melting point of $Cr_2O_3$ has been redetermined to be 2,275° ± ° C.

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## I. INTRODUCTION

A dilute solution of $Cr_2O_3$ in $Al_2O_3$ has long been known as the uby. More concentrated solutions do not possess the desirable lor of the ruby, but are of interest because of their refractory roperties.

Duboin[1] reported that on heating mixtures of $Cr_2O_3$ and $Al_2O_3$ a "red white" heat, from 15 to 16 per cent $Cr_2O_3$ united with the $l_2O_3$. Passerini[2] made an examination by X rays of mixtures which ad been heated to 600° C. and found that limited solution in the olid state occurred at this temperature.

## II. MATERIALS AND GENERAL PROCEDURE

A homogeneous solution of "C. P." $Cr_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$ nd $Al_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$ in warm water was treated with an xcess of ammonium hydroxide. ince both hydroxides are very in-oluble a thoroughly mixed preci-itate is obtained in this way and ixtures of known composition ould be made from weighed mounts of the salts. The washed nd filtered hydroxides were nited to oxides in a platinum rucible over a Méker burner.

The melting temperatures of hese mixtures were determined by eans of an iridium button (fig. 1) eated by high frequency induc-ion. A small piece of the material, bout one-half millimeter in size, as placed in the central hole and overed with a larger piece of the same mixture to promote uniform-y of temperature within the space occupied by the small piece. The

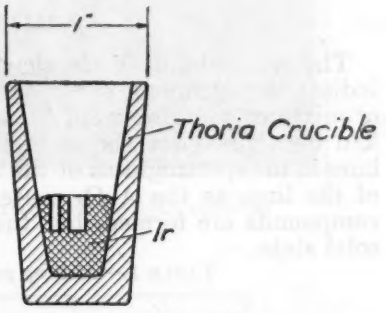


FIGURE 1.—*Crucible with iridium vessel used to obtain temperatures up to 2,300° C. in an oxidizing atmosphere*

[1] Duboin, Compt. rend., 134, p. 840; 1902. [2] Passerini, Gazz. chim. ital., 60, p. 544; 1930.

button was heated to a series of temperatures in steps of 10° C., as measured by an optical pyrometer sighted into the smaller of the two holes in the bu n. After each temperature step the larger piece of material was removed from the cold button and the smaller piece examined with a magnifying glass. An error of 10° or more is possible in judging the condition of partial melting. The calibration of the optical pyrometer was checked before and after these observations were made, and the results are probably accurate within ±25° C.

The temperature of complete fusion was obtained by observing two or three very small pieces of a mixture in the hole as the temperature was raised. Mixtures containing up to 30 mole per cent $Cr_2O_3$ readily "wet" the iridium on melting, while those with high $Cr_2O_3$ content did not, so that the temperature of complete melting of the high $Cr_2O_3$ mixtures could not be determined accurately.

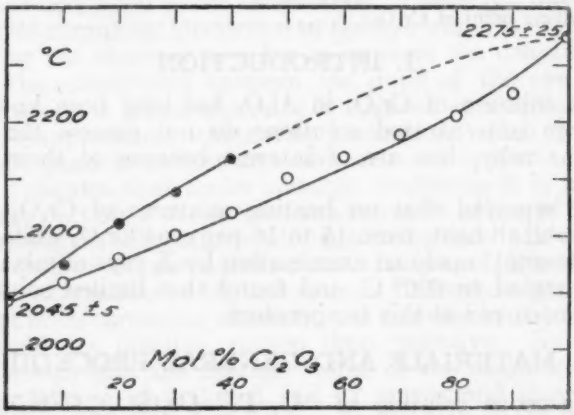


FIGURE 2.—*Phase diagram for the system $Cr_2O_3$-$Al_2O_3$*

## III. RESULTS

The data obtained are shown in Table 1 and Figure 2. They indicate a continuous series of solid solutions. X-ray spectrograms[1] of mixtures containing 20, 40, and 70 mole per cent $Cr_2O_3$ and which had been fused are shown in Figure 3. The absence of additional lines in the spectrograms of the mixtures and the progressive shifting of the lines as the $Al_2O_3$ content is increased demonstrate that no compounds are formed, but that complete miscibility occurs in the solid state.

TABLE 1.—*Melting points of $Cr_2O_3$-$Al_2O_3$ mixtures*

| Mole per cent $Cr_2O_3$ | Solidus temperature | Liquidus temperature | Mole per cent $Cr_2O_3$ | Solidus temperature | Liquidus temperature |
|---|---|---|---|---|---|
| | °C. | °C. | | °C. | °C. |
| 0 | 2,045 | 2,045 | 60 | 2,170 | ---------- |
| 10 | 2,060 | 2,075 | 70 | 2,190 | ---------- |
| 20 | 2,080 | 2,110 | 80 | 2,205 | ---------- |
| 30 | 2,100 | 2,140 | 90 | 2,225 | ---------- |
| 40 | 2,120 | 2,170 | 100 | 2,275 | 2,275±25 |
| 50 | 2,150 | ---------- | | | |

[1] The X-ray spectrograms were made by the metallurgical division of this bureau.

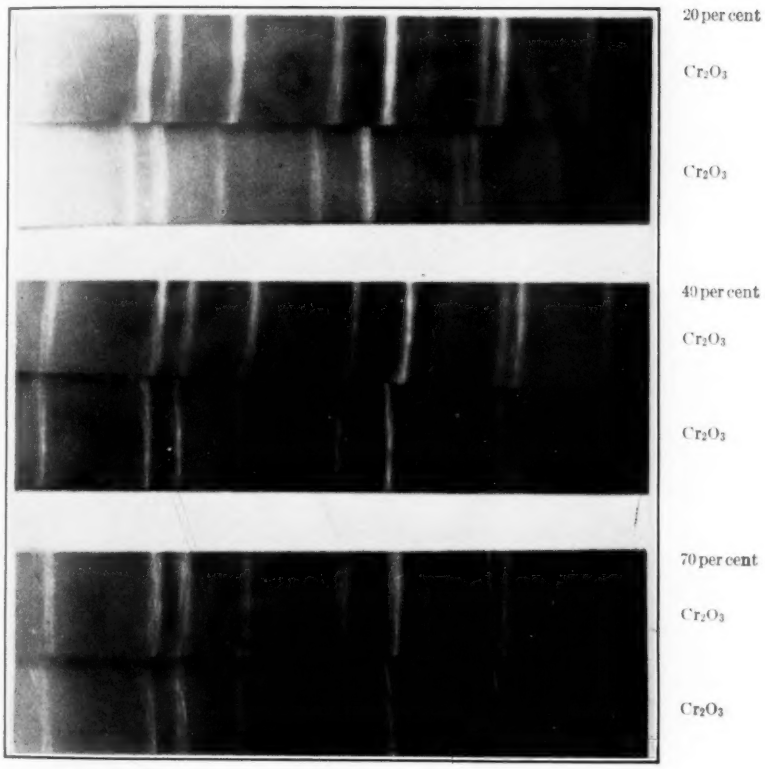


FIGURE 3.—*X-ray spectograms of $Cr_2O_3$-$Al_2O_3$ mixtures*

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## IV. THE MELTING POINT OF $Cr_2O_3$

In a previous paper [4] the melting point of $Cr_2O_3$, which had been prefused in an oxyhydrogen flame, was reported to be 2,140° ± 25° C. As there is a possibility of reducing some of the $Cr_2O_3$ by prefusion in this manner,[5] a sample of unfused $Cr_2O_3$ was prepared from $Cr_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$. The melting point of this unfused $Cr_2O_3$ was found to be 2,275° ± 25° C., as determined in the iridium button. The vapor pressure of $Cr_2O_3$ at this temperature must be considerably under atmospheric pressure, as small pieces kept at this temperature for several minutes did not evaporate from the hole in the button. Wartenberg and Werth could not obtain the melting point of $Cr_2O_3$ in a zirconia furnace, fired with oxygen and atomized oil, because of excessive vaporization above 2,200° C., and concluded that $Cr_2O_3$ sublimed before reaching its melting point. In the presence of reducing gases, which would diffuse through a zirconia tube at this temperature, the $Cr_2O_3$ may have been reduced and vaporized as the metal or a lower oxide, since $Cr_2O_3$ is very susceptible to reduction at high temperatures.

WASHINGTON, March 19, 1931.

[4] Bunting, B. S. Jour. Research, **5**, p. 325; 1930.
[5] Wartenberg and Werth, Zeit. anorg. allgem. Chem., **190**, p. 183; 1930.

# MEASUREMENTS OF EXTREME ULTRA-VIOLET SOLAR RADIATION USING A FILTER METHOD

By W. W. Coblentz and R. Stair

ABSTRACT

In this paper quantitative measurements are given of the component of ultra-violet solar radiation of wave lengths less than 313 mμ.

The method used is a type of filter radiometry, employing a nonselective thermocouple receiver, permanently covered with a filter that is highly transparent to short wave length ultra-violet radiation and practically opaque to the visible and the infra-red rays. By temporarily placing in the path of the rays first one, then two screens of barium flint glass which is opaque to wave lengths less than 313 mμ, the ultra-violet of wave lengths less than 313 mμ is evaluated by exclusion from the total ultra-violet measured.

Measurements are given of the incident ultra-violet solar radiation on the clearest days, as affected by atmospheric pollution, altitude of the station, humidity, time of the day, and season of the year. These data are discussed and correlated with some of the measurements and calculations made by others.

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## I. INTRODUCTION

The present communication is a further contribution to the general subject of instruments and methods of radiometry, that has been under investigation for some years (1).[1] The particular problem considered, which is still under investigation, is the quantitative measurement of short wave length ultra-violet solar radiation.

The method of observation is by means of a nonselective radiometer, permanently covered with a filter that is highly transparent to the ultra-violet radiation of wave lengths less than 313 mμ (millimicrons, 3130 A) and opaque to practically all of the visible and the infra-red rays. Since this filter transmits ultra-violet of wave lengths longer than 313 mμ, the component of wave length less than 313 mμ, is evaluated by temporarily placing in the path of the incident rays, first one, then two screens of barium flint glass, which exclude these rays from the total ultra-violet measured. In this sense, it is an exclusion method of filter radiometry.

[1] Figures in parenthesis here and throughout the text indicate references given in the Bibliography at the end of this paper.

A pressing question of interest and far-reaching importance is a reliable method for evaluating the amount of ultra-violet radiation in sunlight of wave lengths less than about 313 mμ, which varies with the altitude and latitude of the station, the time of the day, the season of the year, cloudiness, and with the countless variations in atmospheric pollution by dust, smoke, etc., that are encountered in different localities.

This subject was discussed in a previous paper (2) in connection with the transparency of special window glasses for transmitting the short wave length ultra-violet solar radiation, of wave lengths less than about 313 mμ, recognized by biologists as having a specific healing value, particularly in the prevention and cure of rickets.

From the preliminary observations given in the preceding paper (2), it was evident that in order to be of value, measurements obtained by this method, should be made only during cloudless intervals. Such a procedure is not objectionable, and, since no other methods equally promising were available at that time it was decided to give the filter method a trial, extending over an annual cycle in order to include winter and summer weather, at Washington. Measurements were made also at two stations at Flagstaff, Ariz., in order to determine the effect of altitude and humidity.

The data thus obtained contain some interesting information that will be discussed on a subsequent page. In a future communication it is proposed to give similar data obtained by a modification of Method III, previously described (2) in which the thermocouple was covered with only a 1 cm cell of water (with quartz windows) and the ultra-violet radiation of wave lengths less than 313 mμ was excluded by means of a barium flint glass screen, as used in the present investigation.

The modification now under investigation consists in exposing both thermocouple receivers ("hot" and "cold," adjusted radiometrically closer than 1 per cent) to the sun, under which conditions practically no galvanometer deflection is obtained. By covering one thermocouple with the barium flint glass screen and the other receiver with a plate of Corex A glass or quartz (to compensate for reflection of radiation at 365 to 1,400 mμ) the galvanometer deflection, obtained on the simultaneous exposure of the two receivers to the sun, is a measure of the ultra-violet excluded by the flint glass filter. By interchanging the screens, differences in the two thermocouple receivers are eliminated.

The chief difficulty lies in obtaining two screens (one opaque to the ultra-violet and the other transparent to the ultra-violet, of wave lengths less than 313 mμ) having exactly the same transmission for wave lengths beginning at about 365 mμ and extending to about 1,400 mμ. Owing to the large amount of radiation in this spectral region, slight differences in the transmission may cause errors in the radiation measurements that are greater than the ultra-violet component that it is desired to measure.

By covering both receivers with a yellow, Noviol C, glass, differences in transparency of the barium flint glass and the Corex A or quartz screens, between 365 and 1,400 mμ, are determined and deducted from the ultra-violet at wave lengths less than 365 mμ excluded by the barium flint glass filter.

The energy value of the ultra-violet shut out by the filter may be determined directly by calibration of the thermocouple receiver

against a standard of radiation as in the previous measurements (2), or from the total solar intensity, $Q$ (and the reduction factor $F$) as described in the present paper. The results obtained by this new method are in good agreement with the data given in the present paper, from which it appears that reliable results may be obtained by using only one barium flint glass screen. It is a good check on the present data by a widely different method.

If desired, this device can be connected with a recording apparatus, thus obtaining a continuous record as used by Pettit (9). However, owing to the large amount of radiation incident upon the water cell (1.2 g cal./cm²/min. as compared with about 8 per cent of this value when using the herein described ultra-violet filter) care must be taken to avoid heating of the cell. In this respect the present method, in which the ultra-violet filter transmits over 80 per cent of the short wave length ultra-violet (without distortion of the shape of the solar spectral energy curve of wave lengths less than 350 m$\mu$) but transmits only 8 per cent of the total solar intensity, $Q$, seems preferable. The ultra-violet filter is to be used also in the new method when it is not being used to check the present method.

With reference to the data presented in the present paper the measurements obtained in Washington are of particular interest in showing the seasonal variation in ultra-violet radiation that may be expected at a sea-level station which is not subjected to atmospheric pollution by factory smoke, but has to contend mainly with pollution by the combustion products from automobiles, and with the increasing numbers of incinerators and oil burners, in office buildings, apartment houses, and private dwellings, which emit not only smoke but also atomized particles of oil.

In this connection it is relevant to anticipate the discussion of the present observations by citing the measurements of October 8, 1929, when the northwest section of the city of Washington was enveloped in a rather dense low-lying stratum of finely divided particles that absorbed the short wave length ultra-violet rays. The atmosphere was cloudless and windstill, and the stratum of bluish haze was easily discernible, extending to a height of 500 to 1,000 feet. As the sun mounted higher in the sky, it shone through a decreasing thickness of this stratum, and the amount of ultra-violet transmitted was greatly increased. For example, the ultra-violet component measured at 9.15 a. m. was about two times the value measured 15 minutes earlier when the sun's rays traversed a longer path of smoke.

## II. METHOD OF OBSERVATION

As outlined in a previous paper (2) the method used consists essentially in isolating the ultra-violet radiation by a purple glass filter, Corning G986A, which is highly transparent to ultra-violet radiation of wave lengths between 250 and 440 m$\mu$ ($tr$=80 to 81 per cent between 310 and 360 m$\mu$) and measuring the intensity of the transmitted rays by means of a thermocouple (of copper-constantan, in air) having a receiving surface about 2.8 mm in diameter. A water cell of fused quartz, 1 cm in thickness, combined with the purple glass filter, G986A, absorbs all the infra-red rays of wave lengths longer than about 1,400 m$\mu$. A correction is easily obtained for the small amount of infra-red rays, of wave lengths 700 to 1,400 m$\mu$, transmitted by the glass filter.

The ultra-violet solar radiation of wave lengths 290 to 313 mμ is obtained by exclusion, by inserting a plate of barium flint glass (G669, thickness = 3.05 mm) having a transmission of 0.5 per cent at 313 mμ, 49 to 50 per cent at 334 mμ, 85 per cent at 365 mμ, and 90.7 per cent or a trifle higher throughout the visible and infra-red to 1,400 mμ and longer wave lengths. The long wave length limit of the ultra-violet cut-off is taken at (and including) 313 mμ instead of 310 mμ because it is a definite and easily obtained emission line (of the mercury arc spectrum) and, also, because biological action, at least in preventing rickets, terminates practically at this wave length (6).

The complete mounting, on its improvised polar axis, is shown in figure 1. The shutter, *S*, is shown opened to the left. The small aluminum disk, *D*, was used to shield the thermocouple receiver from the direct rays of the sun when measurements were made of the sky radiation. The notches in the diaphragmed opening show the compartments for the water cell and the filters.

The diaphragmed opening (19) was purposely constructed to admit radiation from a solid angle of 45° to the sky, which, by scattering, contributes (6 to 10 per cent or more, Table 2) ultra-violet radiation useful for therapeutic purposes. The whole metal box containing the thermocouple and diaphragmed top was wrapped in white cotton batting in order to provide a highly reflecting, thermally nonconducting medium, to reduce the heating on exposure to sunlight.

The experimental procedure consisted in exposing the copper-constantan thermocouple (permanently covered with the 1 cm cell of water and the purple glass, G986A) to the sun and noting the decrease in the galvanometer deflections when increasing amounts of ultra-violet radiation were shut out (*a*) by one filter, then (*b*) by two filters of barium flint glass, G669. The combination of two samples of glass is used to measure the ultra-violet spectral energy distribution in the region of 313 to 365 mμ, and gives some interesting information regarding the variation in energy in this spectral region, which variation is not necessarily in coincidence with the variation in ultra-violet of wave lengths less than 313 mμ shut out by the first screen.

As a matter of information it is relevant to add that in the Washington measurements an ironclad Thomson galvanometer was generally used; also a high sensitivity d'Arsonval galvanometer having a single swing of about seven seconds. At the Lowell Observatory, Flagstaff, Ariz. (altitude 7,250 feet), and on the San Francisco Peaks (near Flagstaff, altitude 10,500 feet) the greater solar intensity warmed the water cell so rapidly (thus affecting the thermocouple) that it was necessary to use a d'Arsonval galvanometer having a single swing of two to three seconds.

An Ångström pyrheliometer was used to measure the solar radiation intensities at the Flagstaff stations. For the Washington comparisons the solar radiation intensities were kindly supplied by I. F. Hand, of the United States Weather Bureau.

It is to be noted that measurements were made only on apparently cloudless days, or parts of days, when sky conditions remained uniform for an hour or more. By making 20 to 40 readings, in Washington, and about 10 readings at the Flagstaff stations, it was possible to attain an accuracy of 1 per cent or greater. The great variations

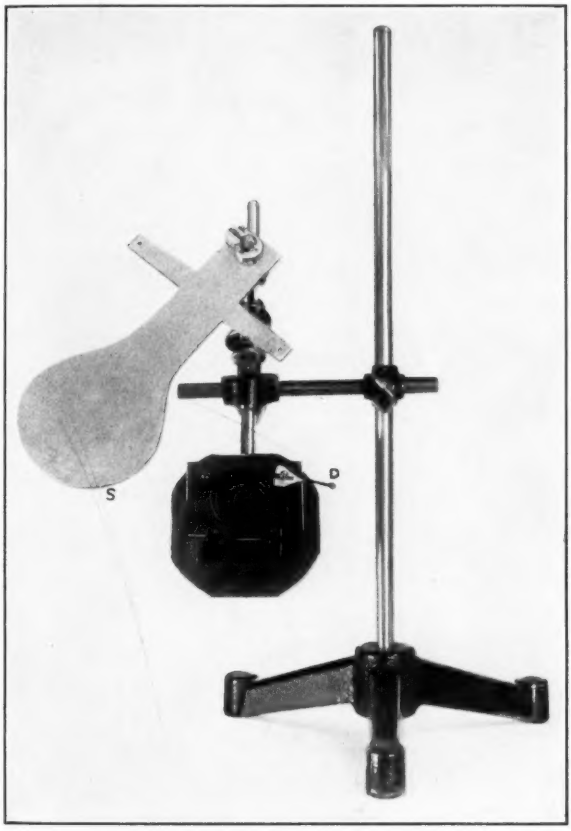


FIGURE 1.—*Front view of ultra-violet radiometer*

The notches in the diaphragmed opening show the compartments for the filters.

in the measurements are, therefore, to be ascribed to atmospheric conditions, which (at sea level) are never stationary as regards transmission of ultra-violet radiation, however uniform the sky may appear to the eye.

This is easily observed with a photo-electric cell that is sensitive only to ultra-violet radiation of wave lengths less than 313 mμ. From their experience with quick-acting photo-electric cells which respond to slight changes in atmospheric transparency, the writers have found it extremely difficult to obtain accurate measurements of the ultra-violet in direct sunlight. This unsteadiness is scarcely noticeable when measuring, with a photo-electric cell, the ultra-violet radiation from wide expanses of the sky. The reasons for these great variations become apparent in going from a low to a high elevation, where the observer becomes aware of the narrow range that obtains in the equilibrium conditions of the temperature and the pressure of the air (at least at certain seasons of the year) as indicated by the sudden appearance, and equally sudden disappearance, of small diaphanous clouds in an otherwise cloudless sky. The temporary condensation of much larger masses of water vapor is necessary in order to be perceptible from a sea-level station. Their presence may be accentuated by looking through a sage green or yellowish green glass.

Owing to the presence of trees that shadowed the laboratory at the noon hour and part of the afternoon in the winter, the observations at Washington are incomplete. However, since there is but little change in air mass at the noon hour in winter, no attempt was made to change the observing station during this investigation.

## III. REDUCTION OF DATA

Using this method of making the measurements it is an easy matter to determine, in arbitrary units, the amount of biologically active ultra-violet radiation shut out by common window glass, and note the variation in amount with change in season, atmospheric pollution, etc.

TABLE 1.—*Ultra-violet solar radiation intensity, u. v. Q. of wave lengths less than 313 mμ, also the total solar radiation intensity, Q, in g cal./cm²/min., for different air masses, m, at Flagstaff, Ariz. (altitude 7,250 feet), and on the San Francisco Peaks (altitude 10,500 feet)*

[The time is Mountain Standard (M. S. T.)]

| Date | Air mass | Q | Screen transmission | | 1.000 minus column 4/column 5 | u. v. Q | Remarks |
|---|---|---|---|---|---|---|---|
| | | | $\frac{a}{I_o}$ | $\frac{a+b}{a}$ | | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 1929 | | *g cal./cm²/min.* | | | | *g cal./cm²/min.* | |
| Sept. 1: | *m* | | | | | | |
| 9 a. m. | 1.81 | 1.28 | 0.857 | 0.893 | 0.040 | 0.000591 | Sky clear over entire hemisphere. |
| 10.35 a. m. | 1.28 | 1.38 | .838 | .887 | .055 | .001010 | Aqueous vapor=8.2 mm. |
| Sept. 5: | | | | | | | |
| 8.30 a. m. | 2.16 | 1.33 | .855 | .888 | .037 | .000511 | Sky perfectly clear at 8 a. m. Cirri appearing at 9 a. m. Sky very blue between clouds. Aqueous vapor=8.1; cloudy p. m. |
| 9 a. m. | 1.80 | 1.38 | .853 | .888 | .039 | .000622 | |
| 10.40 a. m. | 1.29 | 1.52 | .842 | .884 | .047 | .000945 | |

TABLE 1.—*Ultra-violet solar radiation intensity, u. v. Q. of wave lengths less than 313 mμ, also the total solar radiation intensity, Q, in g cal./cm²/min., for different air masses, m, at Flagstaff, Ariz. (altitude 7,250 feet), and on the San Francisco Peaks (altitude 10,500 feet)*—Continued.

| Date | Air mass | Q | Screen transmission | | 1.000 minus column 4/column 5 | u. v. Q | Remarks |
|---|---|---|---|---|---|---|---|
| | | | $\frac{a}{I_o}$ | $\frac{a+b}{a}$ | | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 1929 | | *g cal./cm²/min.* | | | | *g cal./cm²/min.* | |
| Sept. 6: | *m* | | | | | | |
| 11 a. m. | 1.25 | 1.51 | 0.842 | 0.887 | 0.051 | 0.001038 | |
| 11.30 a. m. | 1.18 | 1.51 | .840 | .885 | .051 | .001057 | Cirro-cumulus clouds until 11 a. m., then clear until 2 p. m. and after 4 p. m. Aqueous vapor=6.1 mm. |
| 12.20 p. m. | 1.15 | 1.51 | .835 | .883 | .055 | .001147 | |
| 4 p. m. | 1.85 | 1.38 | .855 | .891 | .041 | .000644 | |
| 4.40 p. m. | 2.25 | 1.25 | .873 | .891 | .020 | .000251 | |
| 5.15 p. m. | 3.12 | 1.19 | .878 | (.891) | .015 | .000139 | |
| Sept. 7: | | | | | | | |
| 11.40 a. m. | 1.19 | 1.55 | .838 | .883 | .051 | .001078 | Fleeting cirri at 11.30 a. m. Sky cloudless in p. m. but thick white haze on western horizon at 5 p. m. Aqueous vapor=4.4 mm at 5 p. m. |
| 1.40 p. m. | 1.21 | 1.54 | .836 | .880 | .050 | .001050 | |
| 4.35 p. m. | 2.24 | 1.28 | .863 | .885 | .025 | .000322 | |
| 5 p. m. | 2.60 | 1.24 | .873 | (.885) | .013 | .000147 | |
| Sept. 9: | | | | | | | |
| 8 a. m. | 2.81 | 1.26 | .883 | .894 | .012 | .000130 | |
| 8.07 a. m. | 2.60 | 1.27 | .872 | (.893) | .024 | .000278 | NE. wind from the Colorado Desert produces "poor seeing." Aqueous vapor=5.0 mm at 9.15 a. m. At 12.17 p. m. clouds and smoke from sawmill cause low value. |
| 8.20 a. m. | 2.30 | 1.32 | .870 | .892 | .025 | .000329 | |
| 8.30 a. m. | 2.20 | 1.35 | .863 | (.890) | .030 | .000414 | |
| 9.30 a. m. | 1.63 | 1.43 | .855 | .884 | .033 | .000572 | |
| 10 a. m. | 1.48 | 1.46 | .847 | .883 | .041 | .000756 | Cirro-stratus over whole sky at 1.30 p. m. |
| 11 a. m. | 1.27 | 1.54 | .841 | (.883) | .047 | .000969 | |
| 12.01 p. m. | 1.18 | 1.53 | .839 | .883 | .050 | .001050 | |
| Sept. 10: | | | | | | | |
| 9.45 a. m. | 1.55 | 1.44 | .852 | (.888) | .041 | .000731 | Slight bluish smoke from sawmill at 10 a. m. Large cirro-cumulus clouds before 9 and after 11 a. m. Aqueous vapor=5.0 mm. |
| 10.15 a. m. | 1.41 | 1.47 | .847 | .888 | .046 | .000872 | |
| 11.15 a. m. | 1.24 | 1.53 | .837 | .882 | .051 | .001051 | |
| Sept. 12: | | | | | | | |
| 1 p. m. | 1.20 | 1.60 | .837 | .880 | .049 | .001115 | San Francisco Peaks. Cloud wisps and more hazy at 1.30 p. m. Large cloud shadow 1.40 to 3.10 p. m. |
| 1.20 p. m. | 1.22 | 1.57 | .840 | .882 | .048 | .001066 | |
| 3.35 p. m. | 1.67 | 1.46 | .853 | (.890) | .041 | .000756 | |
| 3.45 p. m. | 1.80 | 1.44 | .867 | .893 | .029 | .000514 | |
| 4.05 p. m. | 1.93 | 1.38 | .863 | .892 | .032 | .000525 | |
| 4.25 p. m. | 2.25 | 1.36 | .873 | (.892) | .021 | .000316 | |
| Sept. 13: | | | | | | | |
| 9.30 a. m. | 1.67 | 1.42 | .845 | .889 | .050 | .000850 | Sky cloudless all day, but hazy from brush fire 8 to 9 a. m. Smoke from mill at 9.55 a. m. After 11 a. m. sky is clear, blue, no coronal scattering around sun. Aqueous vapor=4.2 mm at 10 a. m., and 3.7 mm at 5 p. m. |
| 9.55 a. m. | 1.51 | 1.45 | .845 | .883 | .043 | .000783 | |
| 11.10 a. m. | 1.27 | 1.55 | .834 | .880 | .052 | .001079 | |
| 12.20 p. m. | 1.20 | 1.54 | .838 | .881 | .049 | .001029 | |
| 2.10 p. m. | 1.28 | 1.48 | .839 | .881 | .047 | .000926 | |
| 2.45 p. m. | 1.43 | 1.47 | .840 | .879 | .045 | .000847 | |
| 4.35 p. m. | 2.28 | 1.31 | .871 | (.889) | .020 | .000261 | |
| 4.50 p. m. | 2.69 | 1.26 | .878 | .889 | .012 | .000133 | |
| Sept. 14: | | | | | | | |
| 11.30 a. m. | 1.23 | 1.64 | .837 | .871 | .039 | .000899 | San Francisco Peaks. Cloudless; sky bluer, less corona than on Sept. 12. Faint clouds appeared at 1.30 p. m., later 50 per cent cloudy. Aqueous vapor=4.5 mm at 7,250 feet. |
| 12.05 a. m. | 1.21 | 1.63 | .837 | .878 | .047 | .001083 | |
| 12.25 a. m. | 1.20 | 1.63 | .833 | .873 | .046 | .001067 | |
| 12.45 a. m. | 1.19 | 1.62 | .834 | .878 | .050 | .001152 | |
| Sept. 16: | | | | | | | |
| 9.50 a. m. | 1.57 | 1.36 | .850 | .883 | .037 | .000619 | In forencon, strong wind from NE., smoky, bluish haze, probably from Colorado desert. Sky cloudless. |
| 11.45 a. m. | 1.22 | 1.47 | .841 | .880 | .044 | .000877 | In afternoon, less wind, sky cloudless; less blue haze on San Francisco Peaks. After 5 p. m. thick whitish haze in SE. and by 6.30 p. m. sky is overcast with thin cirrus clouds. Aqueous vapor=4.0 mm at 8.30 a. m. |
| 12.15 p. m. | 1.20 | 1.47 | .843 | .882 | .044 | .000882 | |
| 2 p. m. | 1.30 | 1.44 | .850 | .882 | .036 | .000686 | |
| 2.15 p. m. | 1.35 | 1.43 | .850 | (.882) | .036 | .000672 | |
| 4.35 p. m. | 2.40 | 1.26 | .870 | .888 | .020 | .000242 | |
| 4.45 p. m. | 2.61 | 1.23 | .878 | .892 | .015 | .000168 | |
| Sept. 19: | | | | | | | |
| 9.30 a. m. | 1.72 | 1.22 | .857 | .890 | .037 | .000533 | At 9 to 9.30 sun shines through thick haze; then distinct cirrus clouds appear. At noon sky is deep blue with large fleeting cirro-cumulus clouds. At 2.30 p. m. sky contains cloud wisps. Aqueous vapor=10.5 mm at 12.30 p. m. |
| 12.01 p. m. | 1.22 | 1.44 | .834 | .883 | .055 | .001073 | |
| 12.15 p. m. | 1.23 | 1.44 | .833 | .881 | .055 | .001073 | |
| 2.35 p. m. | 1.40 | 1.36 | .833 | .886 | .059 | .001034 | |

TABLE 2.—*Ultra-violet solar radiation intensity, u. v. Q, of wave lengths less than 313 mμ, also the total solar radiation intensity, Q, in g cal./cm²/min., for different air masses, m, at Washington, D. C. (altitude 350 feet.)*

[The time is eastern standard (E. S. T.). In column 5 the interpolated values are in parentheses]

| Date | Air mass | Q | Screen transmission | | 1.000 minus column 4/column 5 | u. v. Q | Remarks |
|---|---|---|---|---|---|---|---|
| | | | $\frac{a}{I_o}$ | $\frac{a+b}{a}$ | | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 1929 | | *g cal./cm²/min.* | | | | *g cal./cm²/min.* | |
| Oct. 8: | *m* | | | | | | |
| 9 a. m. | 2.01 | 0.92 | 0.880 | 0.898 | 0.021 | 0.000175 | Sky cloudless all day. Low stratum of blue haze at 8 to 10 a. m. |
| 9.15 a. m. | 1.94 | .99 | .865 | (.893) | .031 | .000285 | |
| 10 a. m. | 1.53 | 1.15 | .868 | .893 | .028 | .000350 | |
| 11 a. m. | 1.46 | 1.24 | .863 | .895 | .036 | .000504 | |
| 12 a. m. | 1.41 | 1.28 | .861 | (.894) | .037 | .000547 | |
| Oct. 9: | | | | | | | |
| 9 a. m. | 2.02 | .69 | .883 | (.895) | .013 | .000080 | Morning clear. Clouds between 9.30 and 11 a. m. Thick haze at noon. |
| 9.15 a. m. | 1.96 | .78 | .880 | (.895) | .017 | .000123 | |
| 12.01 p. m. | 1.43 | 1.11 | .884 | .902 | .020 | .000253 | |
| Oct. 18: | | | | | | | |
| 10.15 a. m. | 1.73 | 1.27 | .863 | .898 | .039 | .000502 | Clear. Cloudless after frost. |
| 11 a. m. | 1.54 | 1.30 | .858 | (.895) | .041 | .000575 | |
| 12.01 p. m. | 1.48 | 1.35 | .863 | .893 | .033 | .000496 | |
| 2.35 p. m. | 2.00 | 1.12 | .867 | (.893) | .029 | .000294 | |
| 3 p. m. | 2.40 | 1.02 | .870 | (.895) | .028 | .000220 | |
| 3.20 p. m. | 2.60 | 1.00 | .880 | (.895) | .017 | .000120 | |
| 3.35 p. m. | 3.00 | .92 | .888 | (.898) | .011 | .000058 | |
| Oct. 19: | | | | | | | |
| 11 a. m. | 1.80 | 1.10 | .869 | (.895) | .027 | .000291 | Clear, cloudless, humid. |
| 11.45 a. m. | 1.50 | 1.14 | .875 | (.895) | .023 | .000290 | |
| Oct. 23: | | | | | | | |
| 9.30 a. m. | 2.00 | 1.19 | .875 | .893 | .021 | .000226 | Sky clear after rain. "City haze" in southeast at 9 to 10 a. m. |
| 10 a. m. | 1.95 | 1.29 | .863 | (.893) | .034 | .000407 | |
| 10.40 a. m. | 1.83 | 1.31 | .864 | (.893) | .033 | .000420 | |
| Nov. 30: | | | | | | | |
| 10.15 a. m. | 2.38 | 1.22 | .879 | (.900) | .023 | .000219 | Sky "good." Temperature 16° F. |
| 10.45 a. m. | 2.27 | 1.23 | .873 | .903 | .033 | .000329 | |
| Dec. 3: | | | | | | | |
| 10.20 a. m. | 2.40 | .96 | .888 | .901 | .015 | .000111 | Sky "poor." Temperature 27° F. windy, sleet on trees. |
| 10.55 a. m. | 2.34 | .97 | .885 | (.901) | .018 | .000137 | |
| Dec. 20: | | | | | | | |
| 9.50 a. m. | 2.97 | 1.15 | .882 | (.898) | .018 | .000120 | Sky clear. Temperature 25° F. at 10 a. m. Ground covered with snow. Sky radiation 6.3 per cent at 10.45 a. m. |
| 10.25 a. m. | 2.49 | 1.24 | .883 | .898 | .017 | .000155 | |
| 10.55 a. m. | 2.37 | 1.27 | .881 | (.898) | .019 | .000188 | |
| Dec. 21: | | | | | | | |
| 9.45 a. m. | 3.00 | 1.17 | .890 | (.898) | .009 | .000060 | Sky cloudless, snow on ground. Temperature 25° F. at 10 a. m. Sky radiation 6.5 per cent at 11 a. m. |
| 10.20 a. m. | 2.48 | 1.22 | .883 | .898 | .017 | .000155 | |
| 10.40 a. m. | 2.40 | 1.25 | .883 | (.898) | .017 | .000164 | |
| 1930 | | | | | | | |
| Jan. 4: | | | | | | | |
| 10.20 a. m. | 2.49 | 1.30 | .886 | .897 | .012 | .000115 | Sky cloudless, light wind. Temperature 34° F. at 10.30 a. m. |
| 10.50 a. m. | 2.44 | 1.36 | .881 | (.897) | .017 | .000174 | |
| Jan. 6: | | | | | | | |
| 9.40 a. m. | 3.06 | 1.12 | .887 | (.898) | .012 | .000074 | Frosty morning. Sky cloudless in a. m. Temperature 40° F. at 10.30 a. m. Sky radiation 7.2 per cent at 10.45 a. m. |
| 10 a. m. | 2.80 | 1.16 | .892 | .898 | .007 | .000052 | |
| 10.30 a. m. | 2.47 | 1.18 | .878 | (.896) | .020 | .000176 | |
| 10.55 a. m. | 2.40 | 1.20 | .873 | .894 | .024 | .000222 | |
| 11.15 a. m. | 2.34 | 1.21 | .864 | (.894) | .033 | .000314 | |
| Feb. 10: | | | | | | | |
| 10.15 a. m. | 2.05 | 1.346 | .871 | (.895) | .027 | .000322 | Morning sky cloudless. Faint cirrus at 11.15 a. m. Sky radiation 7.6 per cent at 11 a. m. |
| 10.30 a. m. | 1.99 | 1.355 | .865 | .895 | .033 | .000404 | |
| 10.45 a. m. | 1.94 | 1.358 | .863 | (.895) | .036 | .000454 | |
| 11.30 a. m. | 1.75 | 1.366 | .865 | (.895) | .034 | .000466 | |
| Mar. 13: | | | | | | | |
| 9.05 a. m. | 2.16 | .978 | .887 | .899 | .013 | .000109 | Sky cloudless, more hazy at 11.50. Very hazy in p. m. Sky radiation 10.2 per cent at 11 a. m. |
| 9.25 a. m. | 1.87 | 1.002 | .873 | (.896) | .026 | .000249 | |
| 9.55 a. m. | 1.64 | 1.043 | .873 | (.896) | .026 | .000281 | |
| 10.45 a. m. | 1.48 | 1.144 | .869 | .893 | .027 | .000344 | |
| 11.50 a. m. | 1.36 | 1.151 | .869 | (.893) | .027 | .000367 | |
| Mar. 15: | | | | | | | |
| 9.25 a. m. | 1.84 | 1.054 | .871 | (.895) | .027 | .000274 | Sky cloudless in a. m. |
| 10.05 a. m. | 1.59 | 1.131 | .871 | (.895) | .027 | .000324 | |
| 10.25 a. m. | 1.51 | 1.153 | .861 | .894 | .037 | .000471 | |
| 11.25 a. m. | 1.36 | 1.198 | .861 | (.894) | .037 | .000523 | Sky radiation 10.8 per cent at 11.15 a. m. |
| 11.55 a. m. | 1.33 | 1.207 | .860 | (.894) | .038 | .000545 | |

TABLE 2.—*Ultra-violet solar radiation intensity, u. v. Q, of wave lengths less than 313 mμ, also the total solar radiation intensity, Q, in g. cal./min./cm² for different air masses, m, at Washington, D. C. (altitude 350 feet)*—Continued

| Date | Air mass | Q | Screen transmission $\frac{a}{I_o}$ | Screen transmission $\frac{a+b}{a}$ | 1.000 minus column 4/column 5 | u. v. Q | Remarks |
|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 1929 | | *g cal./cm²/min.* | | | | *g cal./cm²/min.* | |
| Mar. 20: | *m* | | | | | | |
| 9.05 a. m. | 2.00 | 1.104 | 0.869 | (0.896) | 0.030 | 0.000299 | Sky cloudless in a. m. Sky radiation 7.6 per cent at 11.50 a. m. |
| 10 a. m. | 1.58 | 1.224 | .865 | .896 | .035 | .000459 | |
| 10.35 a. m. | 1.48 | 1.242 | .857 | (.895) | .043 | .000595 | |
| 11.35 a. m. | 1.37 | 1.274 | .859 | (.895) | .040 | .000597 | |
| 11.55 a. m. | 1.31 | 1.281 | .853 | .893 | .045 | .000690 | |
| Apr. 11: | | | | | | | |
| 10.15 a. m. | 1.31 | .87 | .881 | .897 | .028 | .000292 | Thick haze with cirri at 10.40 a. m. to 12.15 p. m. Temperature 75° F. Sky radiation 17.0 per cent at 10.30 a. m. |
| 12.20 p. m. | 1.20 | .90 | .869 | (.897) | .031 | .000346 | |
| 2.45 p. m. | 1.58 | .64 | .881 | (.897) | .028 | .000192 | |
| Apr. 12: | | | | | | | |
| 9.20 a. m. | 1.55 | .52 | .885 | .902 | .019 | .000107 | Thick haze; forest fires on Apr. 11 and 12. Sky radiation 19.0 per cent at 1.05 p. m. |
| 10 a. m. | 1.35 | .74 | .874 | (.900) | .029 | .000253 | |
| 1.15 p. m. | 1.24 | .78 | .875 | .898 | .026 | .000246 | |
| May 3: | | | | | | | |
| 9.05 a. m. | 1.42 | 1.29 | .850 | .887 | .042 | .000622 | Sky cloudless; clearer in p. m. Sky radiation 8.8 per cent at 9.35 a. m.; 8.2 per cent at 10.55 a. m. |
| 10.05 a. m. | 1.36 | 1.30 | .845 | (.887) | .047 | .000721 | |
| 11.05 a. m. | 1.24 | 1.31 | .841 | .889 | .054 | .000858 | |
| 12.05 p. m. | 1.20 | 1.32 | .843 | (.889) | .052 | .000850 | |
| 1.40 p. m. | 1.29 | 1.30 | .849 | (.890) | .046 | .000716 | |
| 2.20 p. m. | 1.36 | 1.29 | .855 | .890 | .039 | .000594 | |
| May 5: | | | | | | | |
| 9.15 a. m. | 1.40 | 1.05 | .875 | .893 | .020 | .000243 | Sky thick, hazy; forest fires. Sky radiation 11.6 per cent at 10.30 a. m. More hazy than May 3. |
| 9.45 a. m. | 1.37 | 1.13 | .876 | (.893) | .019 | .000252 | |
| 10.40 a. m. | 1.26 | 1.18 | .863 | (.893) | .034 | .000487 | |
| 11.55 a. m. | 1.20 | 1.20 | .859 | (.893) | .038 | .000565 | |
| May 10: | | | | | | | |
| 9.15 a. m. | 1.38 | 1.12 | .860 | (.892) | .036 | .000469 | Sky cloudless all day. Light SE. wind. Sky radiation 9.2 per cent at 10.35 a. m.; sky radiation to WSW. 1.9 per cent; zenith, 3.3 per cent at 10.50 a. m., to SE. 2.6 per cent at 3.15 p. m. |
| 10 a. m. | 1.34 | 1.20 | .860 | .892 | .036 | .000510 | |
| 10.55 a. m. | 1.23 | 1.23 | .848 | (.892) | .049 | .000736 | |
| 12.02 p. m. | 1.19 | 1.27 | .846 | .886 | .045 | .000708 | |
| 12.20 p. m. | 1.20 | 1.26 | .847 | (.886) | .044 | .000687 | |
| 1.50 p. m. | 1.33 | 1.26 | .850 | (.883) | .037 | .000554 | |
| 2.25 p. m. | 1.36 | 1.25 | .855 | .883 | .032 | .000472 | |
| June 2: | | | | | | | |
| 9.30 a. m. | 1.25 | 1.22 | .858 | (.890) | .036 | .000533 | Sky cloudless in a. m. Sky radiation 7.5 per cent at 10.30 and 7.8 per cent at 11.30 a. m. Sky SW. 2.8 per cent (altitude 40°). Ratio $a+I_0$ for SW. sky=0.78 to 0.81 showing greater amount of ultra-violet. Thick cirri at 2.10 p. m. |
| 9.55 a. m. | 1.18 | 1.32 | .853 | .890 | .042 | .000691 | |
| 12.10 p. m. | 1.05 | 1.30 | .845 | (.890) | .051 | .000871 | |
| 2.05 p. m. | 1.13 | 1.28 | .852 | (.890) | .043 | .000700 | |
| June 3: | | | | | | | |
| 9.55 a. m. | 1.24 | 1.27 | .855 | (.887) | .036 | .000555 | Sky cloudless. Temperature 86° F. at noon. Sky radiation 8.1 per cent at 11.45 a. m. |
| 10.15 a. m. | 1.11 | 1.33 | .850 | .887 | .042 | .000720 | |
| 11.10 a. m. | 1.07 | 1.35 | .847 | (.887) | .045 | .000794 | |
| 12.01 p. m. | 1.05 | 1.37 | .845 | .887 | .047 | .000835 | |
| 1.30 p. m. | 1.10 | 1.32 | .849 | (.887) | .043 | .000731 | |
| July 7: | | | | | | | |
| 9.45 a. m. | 1.40 | 1.19 | .853 | .884 | .035 | .000481 | Sky cloudless after heavy rain. |
| 10.30 a. m. | 1.21 | 1.23 | .844 | (.884) | .045 | .000686 | |
| July 19: | | | | | | | |
| 9.10 a. m. | 1.42 | 1.06 | .870 | .893 | .026 | .000316 | Fine cirri SE. of sun. Sky radiation 10.1 per cent at 10.45 a. m. |
| 10.20 a. m. | 1.25 | 1.14 | .850 | .890 | .045 | .000623 | |
| 10.35 a. m. | 1.22 | 1.19 | .850 | .887 | .042 | .000615 | |
| July 21: | | | | | | | |
| 10.35 a. m. | 1.23 | 1.09 | .857 | .892 | .039 | .000519 | Sky hazy. Hot. 100° F. Sky radiation 16.5 per cent at 10.50 a. m. |
| 11.00 a. m. | 1.17 | 1.13 | .859 | (.892) | .037 | .000525 | |
| 11.40 a. m. | 1.10 | 1.16 | .861 | (.892) | .035 | .000523 | |
| July 25: | | | | | | | |
| 10.35 a. m. | 1.24 | 1.17 | .850 | (.890) | .045 | .000639 | Sky clear; hot, 98° F. at noon. Sky radiation 8.3 per cent at 11 a. m. |
| 10.50 a. m. | 1.17 | 1.21 | .852 | .890 | .043 | .000653 | |
| 11.45 a. m. | 1.09 | 1.23 | .844 | (.890) | .052 | .000825 | |
| Aug. 12: | | | | | | | |
| 9.20 a. m. | 1.40 | 1.22 | .857 | .886 | .033 | .000465 | Forenoon sky cloudless. Thick haze in west and south horizon at noon. Cool, 72° F. at noon. Sky radiation 7 per cent at 11 a. m. |
| 9.35 a. m. | 1.38 | 1.23 | .852 | (.886) | .038 | .000544 | |
| 10.20 a. m. | 1.21 | 1.27 | .846 | (.886) | .045 | .000708 | |
| 11.05 a. m. | 1.14 | 1.27 | .842 | .890 | .054 | .000866 | |
| 11.30 a. m. | 1.11 | 1.28 | .854 | (.890) | .041 | .000676 | |
| 11.58 a. m. | 1.10 | 1.28 | .851 | (.890) | .044 | .000726 | |

The difficulty arises in expressing these relative values in absolute units of energy. No screen or filter is available that has a sharply defined cut-off at a definite wave length. The effective cut-off of one screen that is opaque to wave lengths less than 310 mμ (for example, the barium flint screens used in this work, which has the sharpest cut-off yet found) ranges from about 338 mμ for air mass, $m=1$ to 341 mμ for $m=3$. This, of course, was known at the beginning of the investigation and recently it has been discussed in print (3).

Owing to the fact that the effective cut-off does not coincide with the long wave-length limit (about 313 mμ) of the biologically active ultra-violet radiation, the observed values (in per cent of the total in column 6 of Tables 1 and 2) obtained by this exclusion method of radiometry, are larger than the true values. The difference between these two values could be determined from a knowledge of the solar spectral energy curve using only one filter. Unfortunately, the ultra-violet spectral energy curve, even for average atmospheric conditions is not well known, and in the spectral region of wave lengths less than 313 mμ it is in greater doubt than for wave lengths 313 to about 365 mμ (the latter value being the long wave length limit concerned in the barium flint screen measurement).

In order to obviate these difficulties to some extent, measurements were made with one ($a$) and with two, ($a+b$) filters of barium flint glass interposed; the latter to determine the percentage of radiation of wave lengths longer than 313 mμ transmitted by the first glass.

As will be noted presently. for the sea-level station, there is a reasonably close agreement between the observed and the computed transmissions. (See fig. 3.) For the higher elevations there is considerable divergence between the calculated and the observed transmissions. (See fig. 4.)

Another difficulty in evaluating the ultra-violet component of solar radiation at 295 to 313 mμ, based upon calculations using the spectral energy curve of the sun, is owing to the fact that, in all such calculations, a smooth energy curve is used, whereas the observed curve is deeply indented by absorption bands. Moreover, the spectral energy curve in the ultra-violet, especially of wave lengths less than 313 mμ is greatly affected by slight changes in atmospheric pollution. This is well illustrated in the transmission measurements of solar radiation through one filter of barium flint glass, which values vary greatly from day to day (as compared with the transmissions of the second filter) for solar radiation of wave lengths longer than 313 mμ that has passed through the first filter, which values vary but little with change in air mass and atmospheric pollution. Hence, as already indicated, the second filter is useful not only in measuring the ultra-violet energy between 313 mμ and about 365 mμ; but, since the ultra-violet cut-off is not sharply defined, it is useful also in obtaining a factor for eliminating the amount of ultra-violet of wave lengths longer than 313 mμ included in the measurement of the ultra-violet of wave lengths less than 313 mμ, obtained with the single filter. This fact, as already stated, was recognized from the start, but the complete correction was not included in the previous paper (2) where only the upper limiting value of the ultra-violet (in per cent of the total) was derived.

The solar spectral energy curves used in the present calculations of the Washington data were taken from the Smithsonian Physical Tables, supplemented in the extreme ultra-violet by the data pub-

lished by O'Brien, by Fabry, and Buisson (4) and by Greider and Downs (5).

The manner of obtaining the ultra-violet radiation of wave lengths less than 313 m$\mu$, by means of this 2-screen method, is illustrated in Figure 2 in which curve $A$ is the observed solar spectral energy curve ($m=1$); curve $B$ gives the spectral energy distribution, $I_0$, after passing through the Corning glass filter, G986A; curve $C$ shows the spectral energy distribution after transmission through one plate of barium flint glass (G669,$a$) and curve $D$ shows the spectral energy distribution after passing through the two filters (G669,$a+b$).

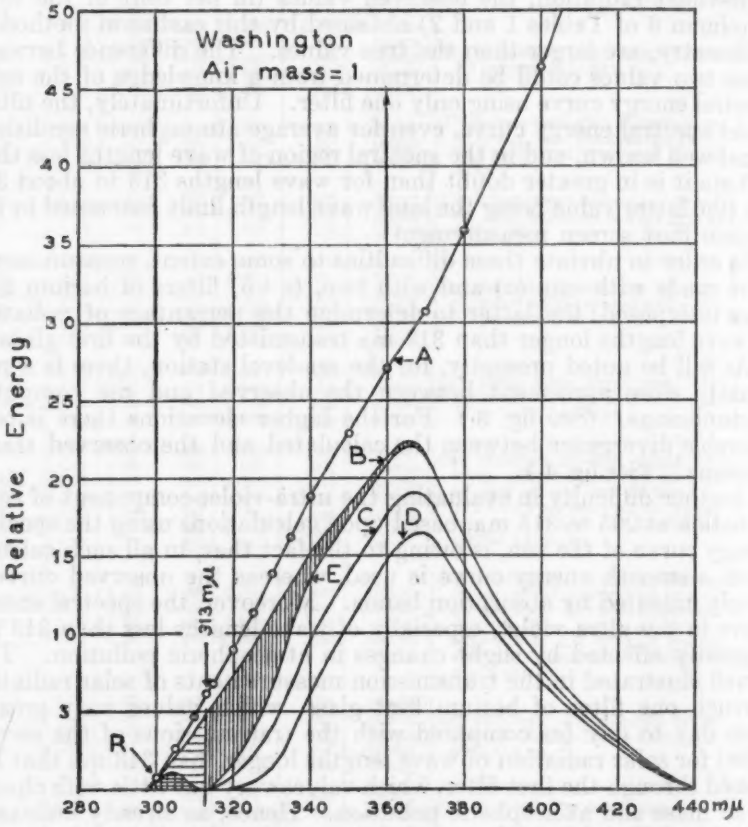


FIGURE 2.—*Graphical method used in reducing the data*

The whole shaded area between curves $B$ and $E$ represents the ultra-violet spectral energy (column 6 in Tables 1 and 2) excluded by this 2-screen method of making the measurement, whereas, the horizontally shaded area, of wave lengths less than 313 m$\mu$, represents the ultra-violet energy that it is desired to evaluate. Incidentally, it may be noted that the effective wave length cut-off, using two screens, occurs at about 329 m$\mu$ for air mass $m=1$ to 330.5 m$\mu$ for $m=3$. It is the sharpest cut-off of all the screens yet tested.

For the sea-level station (Washington, altitude=350 feet) the calculated per cent transmissions for the single barium flint screen,

indicated by the symbol $a/I_o$, and for the two screens, symbol $(a+b)/a$ (fig. 3) are in as close agreement as can be expected. The ratios of observed and calculated values $[a/I_0 : (a+b)/a]$ are in much closer agreement. In view of this close agreement between the calculated and the observed data, it is assumed permissible to calculate suitable factors, $F$, from the average spectral energy curves, in order to reduce the observed measurements (given in column 6 of Tables 1 and 2) represented by the whole shaded area between curves $B$ and $E$, to the energy represented by the horizontally shaded area comprised of wave lengths less than 313 m$\mu$ (shown in fig. 2) which energy, as just mentioned, it is desired to evaluate.

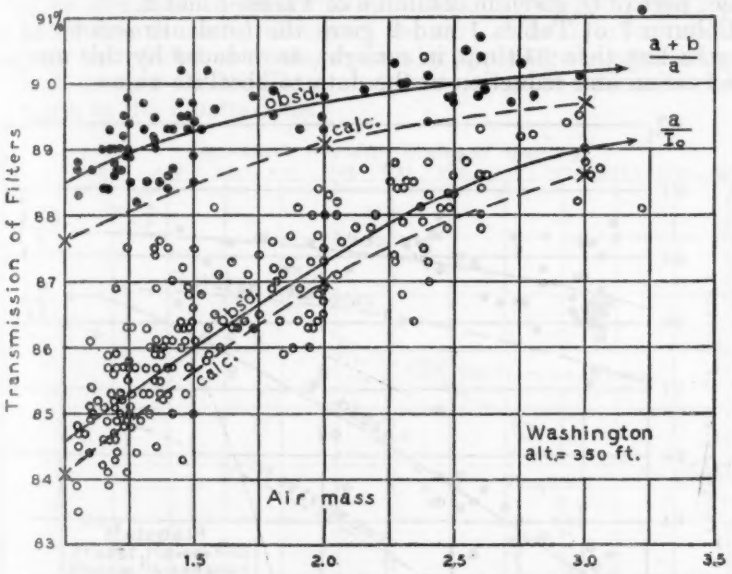


FIGURE 3.—*Observed and calculated transmissions of one and of two standard barium flint glass filters, for different air masses, at Washington, September, 1929, to January, 1931*

These factors, $F$, are obtained graphically from the average solar spectral energy curves, for air masses $m=1$, 2, and 3, in which the area, $I_0$, represents the radiation measured after transmission through the combined filter consisting of the water cell and the purple glass screen, G986A. Similar curves were obtained to represent the spectral transmissions $a/I_0$ and $(a+b)/a$, after insertion of the barium flint screens $a$, and $a+b$. The ultra-violet ends of these curves representing $I_0$, $a/I_0$ and $(a+b)/a$ are shown in curves $B$, $C$, and $D$ in Figure 2.

Since these screens have no selective absorption in the infra-red (which is terminated at 1.4 $\mu$ by the water cell) the determination of the reduction factors, $F$, involves an accurate integration of only the ultra-violet areas of the curves $B$, $C$, $D$, and $E$, and of the shaded area of wave lengths less than 313 m$\mu$, depicted in Figure 2.

These correction factors, $F$, for different air masses are shown graphically in Figure 5, from which curve is taken the value for the particular air mass through which the measurements were made.

The observed amount of ultra-violet shut out by the barium flint glass screens (given in column 6 of Tables 1 and 2; these values are 1.000 − columns 4 ÷ 5) is multiplied by the corresponding factor, $F$ (fig. 5), corresponding with the air mass, $m$, given in column 2 of Tables 1 and 2, in order to obtain the amount of ultra-violet comprised in the band of wave lengths less than 313 mμ.

Since all these values are in terms of the total incident solar radiation intensity, $Q$ (g cal./cm²/min.) and of the transmission factor $K$ (=0.0837) of the combined water cell and glass screen, G986A, the component ultra-violet solar radiation, *u. v.* $Q$., of wave lengths less than 313 mμ is the product of $K.Q.F$ and of the values of the ultra-violet part of $Q$, given in column 6 of Tables 1 and 2.

Column 7 of Tables 1 and 2 gives the total ultra-violet of wave lengths less than 313 mμ, in sunlight, as deduced by this method of observation and reduction of the data to absolute values.

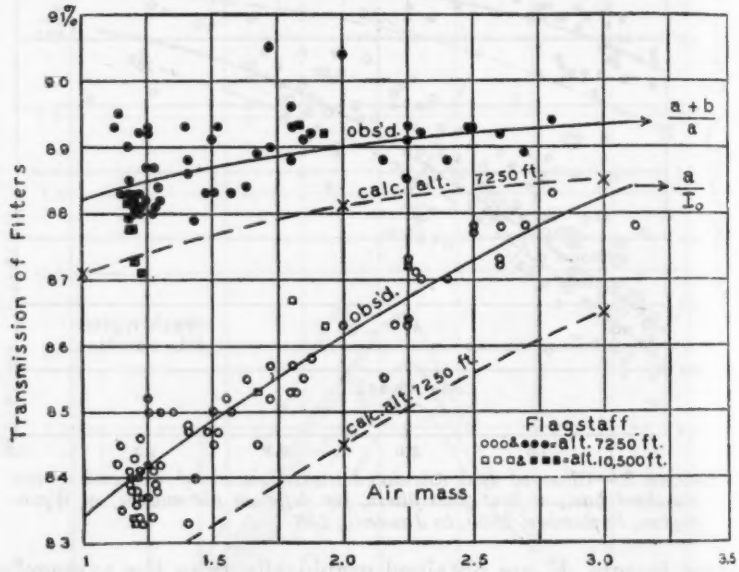


FIGURE 4.—*Observed and calculated transmissions of barium flint glass filters for different air masses, at Flagstaff, Ariz., August to September, 1929*

In view of the great fluctuations in the ultra-violet component from day to day (see figs. 3 and 4), the logical procedure would be to use correction factors, $F$, representing these extremes. However since the corresponding spectral energy curves are not known it seems sufficient to use the average solar spectral energy curve.

As shown in Figure 4 the values of $a/I_0$ and of $(a \div b)/a$, calculated for high elevations, are much lower than the observed values. The ratios of these two measurements are in still greater disagreement with the observed values, indicating that the solar spectral energy curves, used in the calculations, are richer in short wave length ultra-violet radiation than obtains during actual observations. This is entirely different from the conditions at sea level where the observed and the calculated ratios $(a/I_0 : (a+b)/a)$ are in fairly good agreement

The factors, $F$, for reducing the Flagstaff observations to value for the spectral band of wave lengths less than 313 m$\mu$ were, therefore, obtained in the following manner. Instead of air masses the equivalent pressures, in millimeters of mercury (see fig. 5), were plotted against the correction factors, $F$, calculated for Washington (pressure = 760 mm). From this curve were read the correction factors for the two Flagstaff stations (pressures 580 and 500 mm, respectively) for air masses, $m = 1$, 2, and 3.

In view of the fact that the total solar radiation intensity, $Q$, obtained by meteorologists, is in g cal./cm$^2$/min., the present data are given in this unit. The custom among physicists and physiologists is to evaluate thermal radiation flux in radiant power, usually in milliwatts or microwatts ($\mu$w) per cm$^2$. The data in Tables 1 and 2 may be reduced to watts per cm$^2$ by applying the approximate factor 0.07 ($=4.18 \div 60$). They are given in gram-calories and in microwatts in the illustrations.

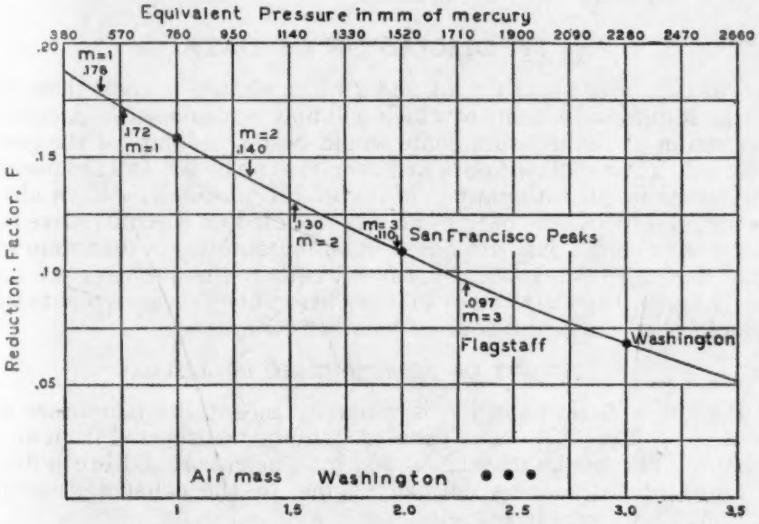


FIGURE 5.—*Reduction factors used in determining the ultra-violet radiation of wave lengths less than 313 m$\mu$*

The data given in column 7 of Tables 1 and 2, represent all the ultra-violet solar energy available in the spectral band of wave lengths less than 313 m$\mu$, generally accepted by biologists as having therapeutic properties, especially in preventing and healing rickets. But the biological effectiveness for equal energy, is not the same for all wave lengths, being a maximum at about 297 m$\mu$, and decreasing to an extremely low value at 313 m$\mu$ (6). The spectral erythemic response curve, for equal energies, observed by Hausser and Vahle, by Luckiesh, Holladay, and Taylor (7) and by the writers (data unplublished) is a maximum at 297 m$\mu$ descreasing to an extremely low value at wave length 313 m$\mu$.

The rubescence curve ($R$ in fig. 2), which is analagous to the luminosity curve of the eye, is the spectral erythemic response curve for an equal energy spectrum multipled by the spectral energy dis-

tribution of the source, which, in this case, is the sun (8). The doubly shaded area under the rubescence curve, $R$, in Figure 2 represents the spectral effectiveness of ultra-violet solar radiation in producing an erythema. The ratio of the shaded area under the rubescence curve $R$, relative to the total shaded area of wave lengths less than 313 $m\mu$, at sea level, is the erythemic efficiency. This ratio does not seem to vary greatly with air mass, the calculated values being 14.5, 14.0, and 12.8 per cent, respectively, for the corresponding air masses, $m=1$, 2, and 3. In other words, the biologically effective ultra-violet component, $R$, is about (14 to 13 per cent) one-seventh to one-eighth of the total ultra-violet component, *u. v. Q.*, recorded in column 7 of Tables 1 and 2; or a range of about 8 microcalories per $cm^2$ per minute, for $m=3$ to about 125 microcalories per $cm^2$ per minute for $m=1.05$. Expressed in terms of radiant power these values are approximately 0.6 and 9 microwatts per $cm^2$, respectively, showing the extremely small amount of ultra-violet energy useful for thereapeutic purposes that is contained in solar radiation.

## IV. DISCUSSION OF DATA

The data given in Tables 1 and 2 when plotted to scale show interesting information, some of which will now be discussed. A complete discussion of the measurements would be too tedious for the general reader. The tabulated data and remarks can be left to the specialists interested in phototherapy. Many of the phenomena have already been noted by others, but not always recorded on a quantitative basis. Since the present data are based upon measurements that were made only during the clearest, cloud-free weather, the averages are necessarily higher than the values that are based upon measurements which are obtained during all sorts of weather conditions.

### 1. EFFECT OF ATMOSPHERIC POLLUTION

By atmospheric pollution is generally meant the temporary presence of dust, smoke, etc. The dust may be transported from an arid region. The smoke may be caused by a neighborhood brush fire, by a forest fire, a passing railroad engine, or the exhaust gases from automobiles, "city haze," etc.

Calculations of the sea-level solar spectral energy curve from data obtained at high elevations seems to indicate the presence of a greater amount of ultra-violet than actually observed, just as though there is a local atmospheric pollution not accounted for in the average spectral energy curve. This, of course, is to be expected.

Notable examples of unusual atmospheric pollution by automobiles, which affected the Washington measurements, are October 8 and 23, 1929, when the transmission of short-wave length ultra-violet solar radiation was doubled in the course of about 15 minutes. (See Table 2.) The low value of the total solar radiation intensity, $Q$, and of the ultra-violet component, *u. v. Q.*, observed on October 9, 1929, are equally interesting.

At the Lowell Observatory station on several occasions the measurements were interrupted by smoke from wood that was burned in a sawmill some miles away. The interesting part of the phenomenon was that on one occasion the blue color of the smoke so closely matched the intensely blue color of the sky that, in the bright sunshine, its presence could hardly be distinguished and would have

escaped notice if its had not affected the thermopile readings. (See Table 1, measurements of 9.55 a. m., Sept. 13, 1929.)

The great variation in the ultra-violet component of solar radiation, as a result of variations in sky conditions, are shown in the high altitude observations (fig. 6) and to a greater extent in the observations at Washington. (Fig. 7.) At the latter station, on some days, the ultra-violet component for air mass, $m=1.5$, is not much larger than in the morning and late afternoon of the clearest days, air mass, $m=3$.

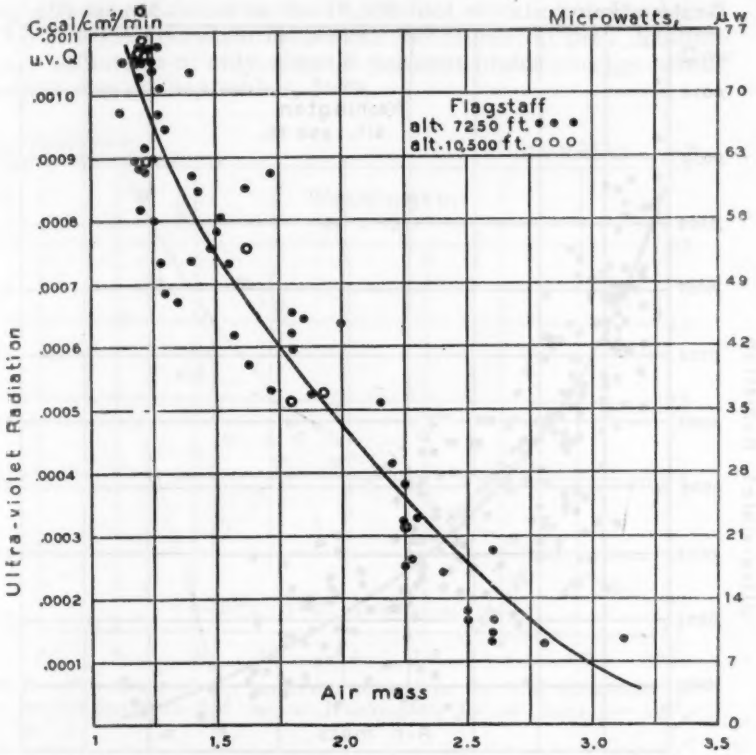


FIGURE 6.—*Total ultra-violet solar radiation of wave lengths less than 313 mμ, in g cal. per cm² per min. (also in microwatts, μw, per cm²), for different air masses at Flagstaff, August and September, 1929*

As is to be expected, for a given air mass, the greater the amount of scattering of the incident rays, the smaller the amount of the directly incident ultra-violet solar radiation, *u. v. Q.* This is illustrated in Figure 8 ($m=1.25$) in which is plotted the total ultra-violet component, *u. v. Q.*, against the per cent of (scattered) "sky radiation," present in the total incident ultra-violet solar radiation measured.

### 2. EFFECT OF ALTITUDE

The effect of altitude on the short-wave length ultra-violet component of sunlight is well known, though quantitative data are not numerous.

Two outstanding factors contribute to the amount of ultra-violet received. The first factor is that, with rise in elevation, the spectral absorption is decreased and the intensity of the short wave lengths, 300 m$\mu$ relative to 320 m$\mu$, is greatly increased. This is indicated in the lower values of the transmission of the barium flint glass screens, $a/I_o$ and $(a+b)/a$, in going from the 7,250 feet elevation to the 10,500 feet elevation.

The second factor is the amount contributed by atmospheric scattering along the path of the incident rays. In this connection Pettit

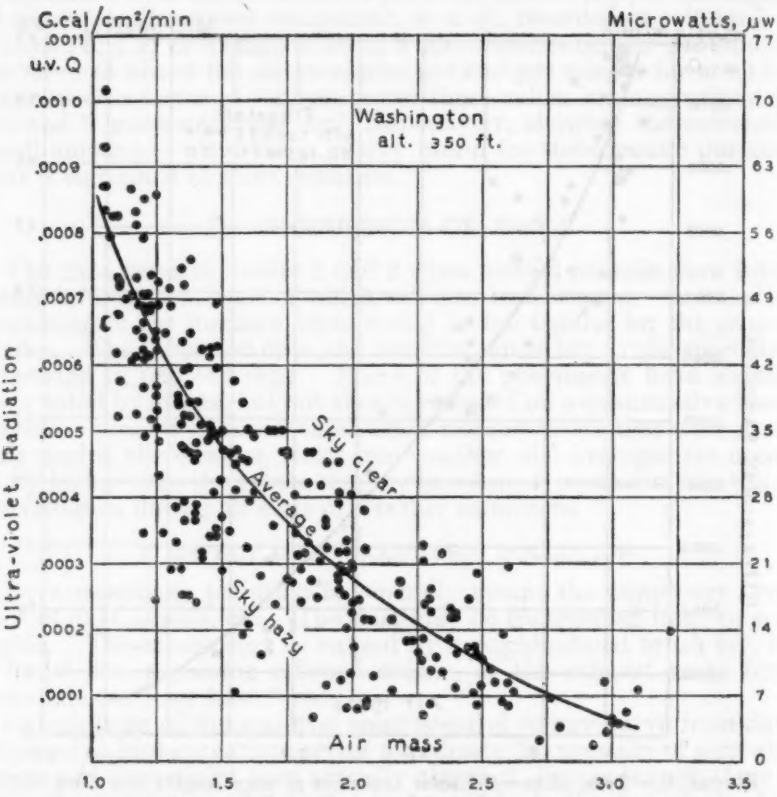


FIGURE 7.—*Total ultra-violet solar radiation, of wave lengths less than 313 m$\mu$, in g cal. per cm² per minute (also in microwatts per cm²), for different air masses at Washington, September, 1929, to January, 1931*

(9) has recently contributed some interesting data, showing that, in going from a sea-level station to a mountain top, the total amount of ultra-violet radiation from the sun increases to some extent, but the ultra-violet scattered by the sky is greatly decreased. His measurements were made at 320 m$\mu$, at which wave length, as shown by the transmission factors $(a+b)/a$, the effect of scattering, with air mass and change in altitude, is less marked than for the shorter wave lengths (at 300 m$\mu$) involved in the present measurements using the single filter, $a/I_o$.

Using a photo-electric cell covered with a film of silver, which transmits ultra-violet of wave lengths at 320 m$\mu$, Pettit (9) found that about 50 per cent of the ultra-violet observed at an elevation of 845 feet was contributed by the sky, while at an elevation of 5,700 feet only about 30 per cent of the total ultra-violet measured was contributed by the sky. On the other hand, the total ultra-violet (sun plus sky) observed at the 5,700-foot elevation was only about 5 per cent greater than at the lower elevation.

These observations are substantiated by the present measurements (see Table 1 and fig. 9) where the total ultra-violet, for $m=1.2$, was *u. v. Q.* = 1,150 microcalories at the 10,500-foot elevation as compared with *u. v. Q.* = 1,080 microcalories per cm$^2$ per minute at the 7,250-foot elevation, a difference of only about 8 per cent under average conditions at that season, September, 1929.

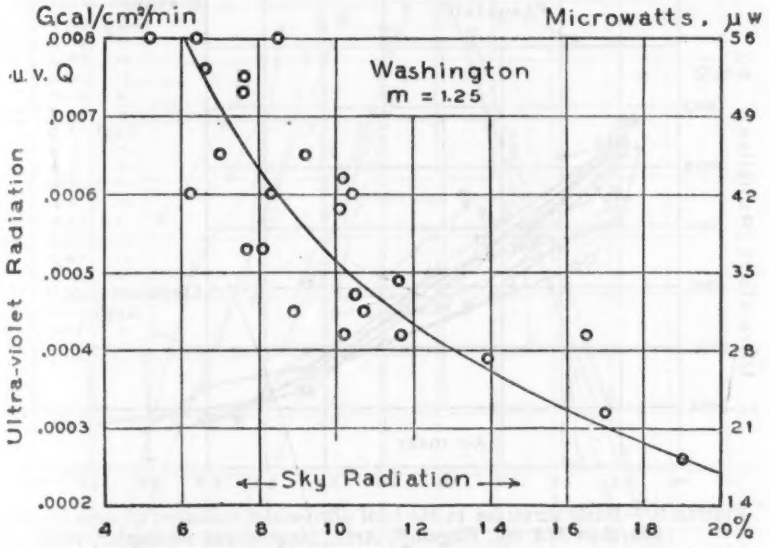


FIGURE 8.—*Percentage of sky radiation present in the total ultra-violet of wave lengths less than 313 m$\mu$, at Washington, for air mass $m=1.25$. (See fig. 7.)*

The greater erythemic effectiveness of the ultra-violet rays, observed at the higher elevation is therefore to be ascribed to the presence of a greater amount of short wave lengths (at 297 to 302 m$\mu$) ultra-violet radiation, as indicated by the lower transmission, $a/I_o$ observed through the barium flint glass filter.

### 3. EFFECT OF HUMIDITY ON SCATTERING

But little information is available regarding the amount of scattering caused by water vapor along the path of the incident radiation.

The Washington measurements (Table 2) show that on the clearest days (absence of smoke and dust) only about 5 per cent of the total *u. v. Q.* is scattered sky radiation, the average being about 10 per cent of the total, rising to 19 per cent on April 12, 1930, as a result of the Shenandoah forest fire.

The most interesting results on the effect of humidity were obtained at the Arizona stations, where observations were begun near the close of the rainy season when the pressure of the aqueous vapor at the 7,250-foot elevation was 10 mm. This was followed by a period of low vapor pressure (4 to 5 mm) which, fortunately for a verification of the earlier observations, was terminated by a day (Sept. 19, 1929, Table 1) of relatively high vapor pressure.

As shown in Figure 10, where the total ultra-violet radiation, *u. v. Q.*, is plotted against the total solar radiation intensity, *Q*, during the period of relatively high vapor pressure, the ultra-violet component, *u. v. Q.*, is distinctly higher for a given value of *Q* (group *A*) than during the period of low vapor pressure (group *B*), so that with a solar intensity of $Q = 1.3$ g cal. the average *u. v. Q.* was as high

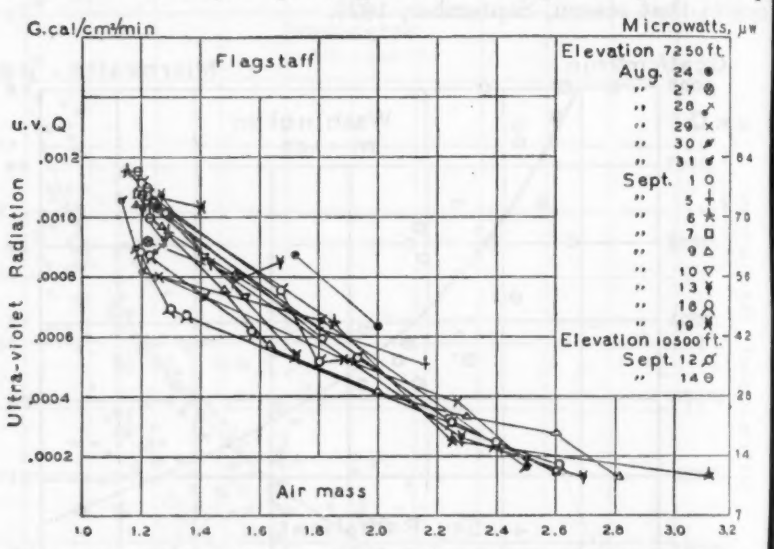


FIGURE 9.—*Daily variation in the total ultra-violet radiation of wave lengths less than 313 mμ, Flagstaff, Ariz., August and September, 1929*

(0.0009 g cal.) as was observed at the low vapor pressures (4 mm) when $Q = 1.5$ g cal. It is to be noted, however, that, while the total ultra-violet component at the 7,250-foot elevation is almost as high as observed at the 10,500-foot elevation, the spectral quality is different, containing a somewhat less amount of the short-wave lengths 290 to 300 mμ. This conclusion follows from the proper interpretation of the transmissions observed with the barium flint glass screens.

It is relevant to add that the effect of humidity upon the total incident solar radiation, *Q*, is well known to meteorologists, the relatively lower values of *Q* in June and July being caused, in part, by the increased amount of water vapor in the atmosphere.

In this connection it is interesting to note the observations of Dannmeyer (17), showing the importance of sky radiation upon the total biologically active ultra-violet incident in high latitudes—Iceland, Finland, Norway, etc. During a period of exceptionally clear weather, at midday, in June and July, the total ultra-violet in direct sunlight in Iceland (measured with a cadmium photo-electric

cell) was never greater than 45 per cent of the *u. v. Q* received from the whole sky. He comments upon the biological effect of this sky radiation upon the natives, living in towns surrounded by basalt walls 400 m high, whose faces, blanched during the long dark winters, show a ruddy hue long before the sun shines directly into the fiords.

### 4. DAILY VARIATION IN ULTRA-VIOLET RADIATION

The daily variation in intensity of the ultra-violet component, *u. v. Q.*, from an imperceptible amount at sunrise and sunset to a maximum at the noon hour is well known and needs but little comment in the present paper.

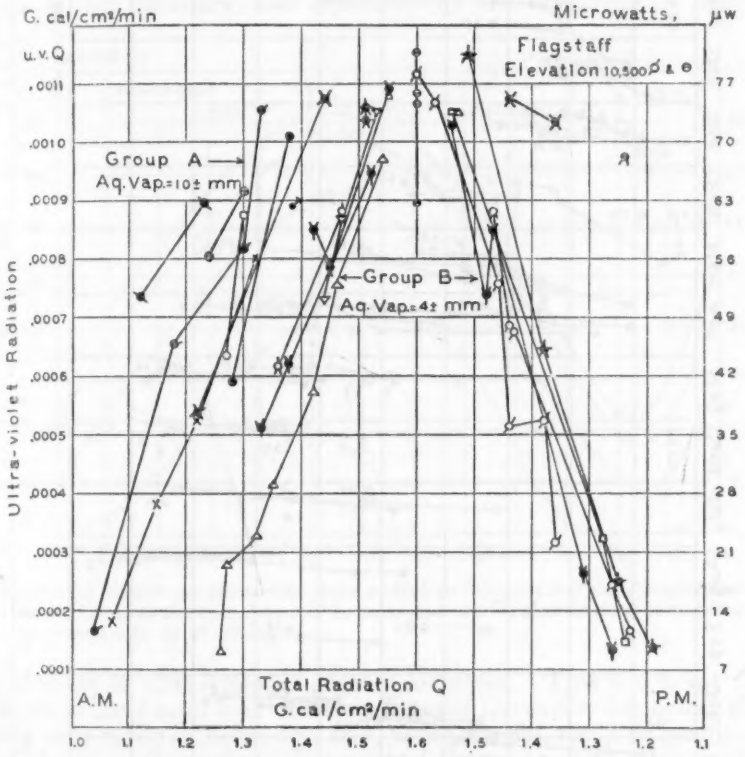


FIGURE 10.—*Daily variation in ultra-violet radiation (u. v. Q) relative to the total incident solar radiation (Q) in g cal. per cm² per minute, at Flagstaff, Ariz., showing the effect of aqueous vapor*

In Figure 10 are depicted some of the measurements of the *u. v. Q.* made at the Flagstaff, Ariz., stations. The Washington measurements (fig. 7), being plotted against air mass, do not distinguish between the forenoon and afternoon observations. However, in both cases, the wide variations in the *u. v. Q.*, throughout the day and on different days, indicate the futility of attempting to specify intensities for average meteorological conditions. Fortunately, common experience shows that the human body is not greatly affected by these variations in intensity, so that a precise dosage meter is not necessary to evaluate the intensities in heliotherapy as now practiced.

## 5. SEASONAL VARIATION IN ULTRA-VIOLET RADIATION

In Figure 11 are plotted the various observations of ultra-violet radiation, *u. v. Q.* at Washington, for different times of the day (different air masses given at the top of fig. 11) during different

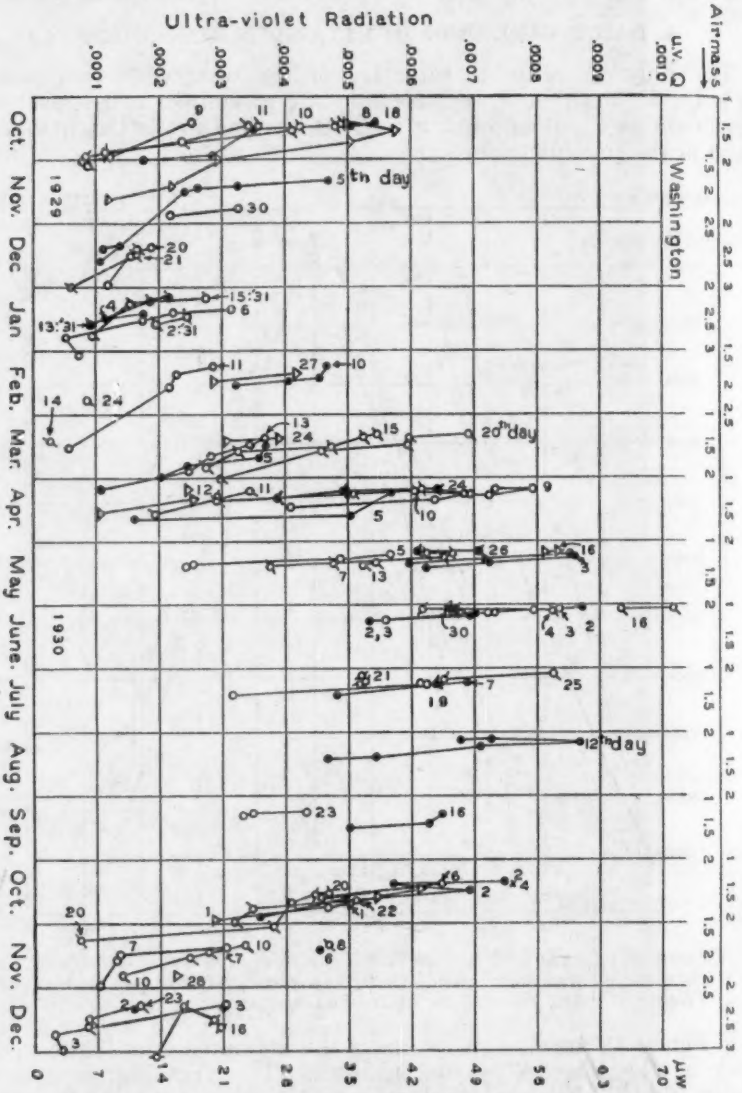


FIGURE 11.—*Daily and seasonal variation in ultra-violet solar radiation of wave lengths less than 313 mμ, in Washington, October, 1929, to December, 1930*

months of the year. The envelope, drawn through the maximum and the minimum values, produces an interesting curve, showing, the well-known periodicity in the intensity, varying from a sharply defined minimum in December to a broadly defined maximum extend-

ing from May to August. No attempt is made to correlate the incident ultra-violet with solar activity (sun spots) which is being investigated by Pettit (9).

In Figure 12 the data are plotted to illustrate the amount of ultra-violet incident at Washington at different hours of the day (usually the forenoon) during the year 1930 and the first part of 1931. The low average values in July are owing to haziness caused by the drought (dust) and forest fires.

As illustrated in Figure 12, the ultra-violet component radiation, *u. v. Q.* of biological importance in sunlight is imperceptibly small before 9 a. m. (and after 3 p. m.) in winter; and only during three to four hours, in the middle of the day does it become of real importance. However, by February, and especially by the beginning of March,

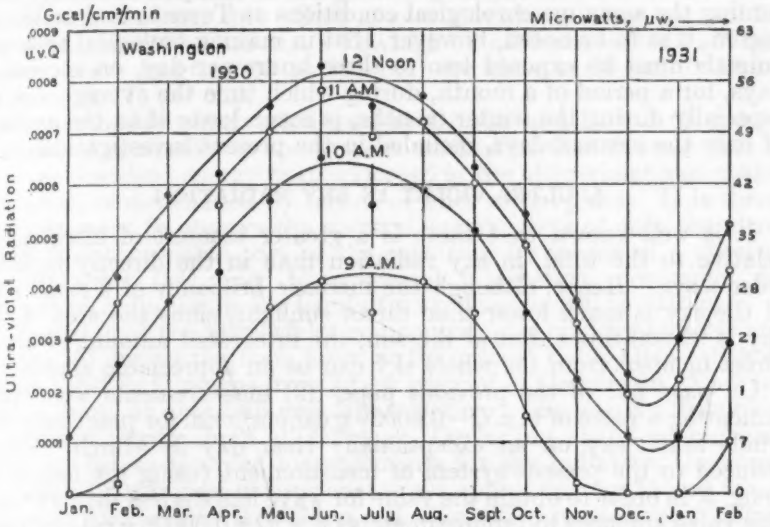


FIGURE 12.—*Average ultra-violet solar radiation intensities of wave lengths less than 313 mμ at the even hours, 9 a. m. to noon on the clearest days throughout the year 1930, in Washington*

the amount of ultra-violet is greatly increased. This is a point that appears to have been overlooked in some of the earlier biological tests which were made in February, and, hence, do not apply to conditions that obtain in December. For even if there are more clear days in December than in January and February, accepting the observations of Russell, Massengale, and Howard (11) that the duration of the effect of a single exposure to ultra-violet radiation upon bone formation in chicks lasts about two weeks, then the biological action obtained on a single clear day in January and February would be far more effective than several days of exposure to the sun, during December.

The foregoing data are interesting in showing that in addition to the daily variation in the intensity of the ultra-violet component, *u. v. Q.*, there is the well-known seasonal variation which is a minimum at the winter solstice, December 22, when at the noon hour on the clearest day, in Washington, the *u. v. Q.* is less than 200 micro-

calories (about 14 $\mu$w) per cm$^2$ or about one-fourth the maximum values at the summer solstice. This value seems to be remarkably high, but it is to be noted that the total amount of ultra-violet, *u.v. Q.*, observed in December is of wave lengths 305 to 313 m$\mu$, especially of the latter wave lengths, which have a low biological action.

If we consider only the energy included under the rubescence curve, *R*, in Figure 2, which equates the spectral energy according to its biological (erythemic) effect, then the maximum biologically active ultra-violet component, *u. v. Q.* calculated from the average solar spectral energy curve, at the winter solstice, is about one-fifth to one-sixth the maximum at the summer solstice.

The biological tests of Tisdall and Brown (10) made at Toronto (latitude 43° 6′), indicate that during the winter months the anti-rachitic effect is about one-eighth as great as in April and May. Assuming the same meteorological conditions at Toronto and at Washington, it is to be noted, however, that in making biological tests the animals must be exposed two to three hours per day, on successive days, for a period of a month, during which time the average *u. v. Q.* especially during the winter months, is much lower than the average of only the clearest days, included in the present investigation.

### 6. ULTRA-VIOLET IN SKY RADIATION

It is well known that there is a greater amount of ultra-violet, relative to the total, in sky radiation than in the directly incident solar ways. Hence, although the intrinsic brilliancy of a small area of the sky is much lower than direct sunlight, since the area of the sky is 92,000 times that of the sun, the integrated amount of ultra-violet incident from the whole sky can be an appreciable amount.

On page 682 of the previous paper (2) measurements were cited indicating a value of *u. v.* $Q = 0.00029$ g cal/cm$^2$/min. for practically the whole north sky on an exceptionally clear day in March. When reduced to the present system of measurement (using the factor, *F*, in fig. 5, in order to obtain the value for wave lengths less than 313 m$\mu$) this value amounts to (approximately) *u. v.* $Q = 0.00006$ g cal/cm$^2$/min. or about one-fifteenth of June sunlight, which is an appreciable amount.

By means of a uranium photo-electric cell, sensitive to wave lengths less than 334 m$\mu$ and the barium flint glass screen, it was found that, of the total intensity measured in foot candles, the light from the north sky contains about 50 per cent more of the biologically active ultra-violet component than direct sunlight. However, since the intensity of skylight that can pass through an average sized window, and shine upon an object 5 m back of the window, is only 10 to 12 foot candles or about 1/800 to 1/1000 of full sunlight, it follows that it would be necessary to expose an object for 14 to 15 hours to receive the same amount of ultra-violet as would be obtained in a 1-minute exposure to direct June sunlight (12).

### 7. COMPARISON OF DATA

As already mentioned, practically all the quantitative data, heretofore available, on the biologically active ultra-violet in sunlight, were derived by calculation from an assumed average spectral energy curve (9, 13) which formed also the basis of one method of attack, previously

used by the writers (2). In the present investigation the average solar spectral energy curve is used merely as a secondary factor for reducing to an absolute energy basis the ultra-violet energy measurements obtained under various atmospheric conditions. While the data obtained by these two methods of attacking the problem are in reasonably good agreement, nevertheless the present measurements show that such comparisons can be used only in a general discussion of the problem, and that in accurate, quantitative biological tests, simultaneous local ultra-violet measurements must be made.

From his analysis of the solar spectral energy curve observed on Mount Wilson, supplemented by measurements with a silvered photoelectric cell that has a maximum response at about 320 m$\mu$, Pettit (9) deduced that the intensity of the ultra-violet component of wave lengths 290 to 310 m$\mu$, in midsummer sunlight amounts to about 70 microwatts ($\mu$w) per cm$^2$. This amounts to about 90 $\mu$w per cm$^2$ for wave lengths 290 to 313 m$\mu$. The highest values observed in Washington (wave lengths 290 to 313 m$\mu$) are close to 70 $\mu$w (0.0010 g cal/min., fig. 7) per cm$^2$.

The method of observation used by Grieder and Downs (5) has an element of similarity to the present method in that the per cent of the total incident energy that is located in the ultra-violet and visible spectrum, is determined by means of filter of red glass. It is therefore necessary to observe the spectral energy curve of only the ultra-violet and the visible part of the spectrum by means of a spectropyrheliometer (14) and, by graphical integration, determine the amount of radiation in the band of wave lengths 290 to 310 m$\mu$.

The value of the ultra-violet component, observed by Greider and Downs (5) during the noon hour, at Springfield Lake, Ohio (altitude about 1,200 feet) ranges from 12 $\mu$w per cm$^2$ in October to 23 $\mu$w per cm$^2$ in June, or about 16 and 30 $\mu$w per cm$^2$, respectively, using the long wave length limit at 313 m$\mu$. Deducting about 10 per cent from the herein-recorded measurements for sky radiation, the corresponding Washington measurements are approximately 35 and 50 $\mu$w per cm$^2$ 0.0005 and 0.00073 g cal. (fig. 12), respectively. Their measurements at Cragmor, Colo. (altitude about 6,500 feet), gave 16 $\mu$w per cm$^2$ in November to 53 $\mu$w per cm$^2$ in June, or 21 and 69 $\mu$w per cm$^2$, respectively, using the long-wave length limit at 313 m$\mu$. Extrapolating the herein-described measurements at Flagstaff, Ariz. (fig. 9), to air mass $m = 1.02$ (June) and deducting 10 per cent for sky radiation gives 77 $\mu$w per cm$^2$ (0.0011 g cal.).

Supplementing these radiometric measurements are the physiological tests of Luckiesh (15) who, from determinations of minimum perceptible erythema and computations of energy between 280 and 310 m$\mu$ produced by a tungsten-filament lamp with a special bulb, concludes that the best midsummer sunlight supplies not less than 25 $\mu$w per cm$^2$ with a probable value of 40 $\mu$w per cm$^2$ of ultra-violet energy shorter than 310 m$\mu$, or 33 and 52 $\mu$w per cm$^2$, respectively, for wave lengths less than 313 m$\mu$.

From the foregoing it appears that the present method of measuring ultra-violet solar radiation gives slightly higher values than the method employed by Greider and Downs, and lower values than obtained by Pettit. The various estimates of the value of ultra-violet solar radiation of wave lengths less than 313 m$\mu$, for mid-latitude sea-level stations, during midday in midsummer, are as follows: Pettit, 90 $\mu$w;

Greider and Downs, 33 $\mu$w (corrected for sky radiation); Luckiesh, 33 to 52 $\mu$w; Coblentz and Stair 55 $\mu$w per cm$^2$ (20).

Considering the variety of methods of attack and of reducing the measurements, and the marked local differences in meteorological conditions at the different stations, these estimates are in as good agreement as can be expected. For, while this general agreement is of interest, the question of primary importance is a quick, reliable, and convenient method of determining, in absolute value, the amount of biologically effective ultra-violet radiation incident at a given station.

Heliotherapists find that the best time of the day to give sunbaths is in the early forenoon (8 to 9 a. m.) and late afternoon in summer, and during the noon hours in winter. From a correlation of their radiometric data with these biological data, Greider and Downs (5) estimate the dosage intensity of "clinical sunlight," used in heliotherapy amounts to about 14 $\mu$w per cm$^2$. On the basis of the present method of observation, which includes wave lengths less than 313 m$\mu$ the dosage unit of "clinical sunshine" is about 20 $\mu$w per cm$^2$. This is considerably smaller than the estimate previously published (8, 2). However, the former estimate was based upon an assumed upper limit of 70 $\mu$w, which is negatived by the results of the present research (20).

## V. SUMMARY AND ACKNOWLEDGMENTS

The present paper is a contribution to the investigation of instruments and methods of radiometry, in particular to the quantitative measurement of the component of ultra-violet solar radiation, of wave lengths less than 313 m$\mu$, which biologists recognize as of especial importance in the prevention and cure of rickets.

The apparatus used consisted of a nonselective radiometer (a thermocouple) permanently covered with a cell of water and glass filter, Corning G986A, which combination is highly transparent to ultra-violet and largely opaque to the visible and the infra-red rays. By temporarily placing a screen of barium flint glass in the path of the incident rays, the ultra-violet of wave lengths less than 313 m$\mu$ is evaluated by exclusion from the total ultra-violet measured.

Observations were made at Washington, D. C. (latitude 38.9°; altitude 350 feet) at the Lowell Observatory, Flagstaff, Ariz. (latitude 35.2°; altitude 7,250 feet) and on the San Francisco Peaks, near Flagstaff (altitude 10,500 feet).

Data are presented on the incident ultra-violet solar radiation as affected by (*a*) atmospheric pollution, (*b*) altitude, (*c*) humidity, (*d*) time of the day, (*e*) season of the year, and (*f*) sky radiation.

Among the outstanding items of interest is the great reduction in intensity of ultra-violet radiation by atmospheric pollution by dust, smoke, and the combustion products of automobiles. This produces a wide variation in the daily and seasonal observations, especially at sea-level stations.

At high elevations the spectral quality of the ultra-violet component is richer in the short wave lengths (295 to 305 m$\mu$) than at sea-level; but owing to atmospheric scattering, the total amount of ultra-violet of wave lengths less than 313 m$\mu$, at sea-level on the clearest days, is almost as large as at high altitudes.

Atmospheric water vapor is an important contributing factor in scattering ultra-violet radiation, that is most easily observed with changes in humidity at high altitudes.

The amount of ultra-violet solar radiation of wave length less than 313 m$\mu$, previously estimated to be 0.3 per cent of the total incident radiation, was an upper limiting value which is now superseded by more complete measurements, made on the clearest days in Washington, indicating noon hour values ranging from about 14 microwatts (200 microcalories per minute) per cm$^2$ in December to about 56 microwatts (800 microcalories per minute) per cm$^2$ in June (20).

Acknowledgements are due to the Lowell Observatory, in particular Dr. C. O. Lampland, for the facilities placed at our disposal, including transportation to the San Francisco Peaks; also to Mrs. W. W. Coblentz for assistance in making the observations in Arizona, and to J. M. Hogue for assistance in making some of the latest observations in Washington. Acknowledgment is due to Dr. H. H. Kimball, of the United States Weather Bureau, for the calibration of the Angström pyrheliometer used at the Flagstaff stations and to I. F. Hand for the numerous data on air masses ($m$) and solar intensities ($Q$) supplied in connection with the Washington measurements of ultra-violet radiation.

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WASHINGTON, February, 21, 1931.

# THE INFLUENCE OF CHEMICAL COMPOSITION AND HEAT TREATMENT OF STEEL FORGINGS ON MACHINABILITY WITH SHALLOW LATHE CUTS

By T. G. Digges


## ABSTRACT

The tests described in this report were made primarily as a study of lathe-tool performance with shallow cuts as affected by variations in chemical composition and heat treatment of the steels cut. The cutting tests were made dry with high-speed steel tools of a selected size, form, composition, and heat treatment, with a feed of 0.0115 inch per revolution and 0.010 inch depth of cut. Comparisons were made of the Taylor speeds on the basis of equal tensile strengths when cutting 0.4 per cent carbon (S. A. E. 1040), chromium-vanadium (S. A. E. 6140), nickel-chromium (S. A. E. 3140 and 3435), chromium-molybdenum (S. A. E. 4140), and 3½ per cent nickel (S. A. E. 2340) steel forgings heat treated to give tensile strengths between 75,000 and 220,000 lbs./in.²

This study also included consideration of the surface finishes of the various steel forgings as affected by the test conditions, the microstructures of the steels cut, and tool performance as affected by the additions of 3.5 to 11.7 per cent cobalt to the customary 18 per cent tungsten type of high-speed tool steel.

If machinability is measured by the cutting speed permitting the tools to last a definite time, then measurable differences were observed between the various steels cut in the lathe test with shallow cuts. The fact, however, that some given steel permits a higher cutting speed than another steel for some tensile strength which is the same for both materials does not necessarily indicate that the two steels maintain the same relationship for another tensile strength.

Of the different steels cut in the lathe tests the plain carbon steel was the most difficult to machine other than an annealed nickel-chromium steel. The surface finish on the plain carbon steel was also considered to be inferior to that of the alloy steels.

The results showed that the effect of changes in chemical composition of steel forgings upon their cutting speeds was dependent upon the tensile strength at which the comparisons were made. In the different steels cut with shallow cuts the most effective special alloying elements for improving machinability were the combinations of nickel and chromium or chromium and vanadium for the high tensile strengths in the neighborhood of 180,000 lbs./in.², while chromium and molybdenum were the most effective in the lower range of about 90,000 lbs./in.²


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## I. INTRODUCTION

During the past 10 years a study has been made at the National Bureau of Standards of lathe-tool performance with both roughing and shallow cuts. The lathe breakdown test for roughing cuts was

used in studying the effects upon tool performance of changes in chemical composition and heat treatment of commercial and experimental high-speed steels [1] [2] [3] and of variations in chemical composition and heat treatment of the steels cut.[4] The lathe breakdown test has also been extended to include cutting tests with cemented tungsten carbide tools.[5]

A method for testing lathe tools with shallow cuts was developed and used for studying the effects upon tool performance of changes in chemical composition and heat treatment of the tools. Relations between the cutting speed, feed, and depth of cut and the tool life for carbon and high-speed steel tools were also determined.[6] [7] Most of the tests with shallow cuts were made in cutting 3½ per cent nickel steel forgings, heat treated to have tensile strengths of about 80,000 to 100,000 lbs./in.[2]

The tests described in this report were made primarily as a study of high-speed steel lathe-tool performance with shallow cuts as affected by variations in the chemical composition and heat treatment of the steels cut. The study also included consideration of the surface finishes of the various steel forgings as affected by the conditions of cutting and of the microstructures of the steels cut.

The lathe tests were made in cutting a plain carbon and various alloy steel forgings heat treated to have tensile strengths between 75,000 and 220,000 lbs./in.[2] The form, size, heat treatment, and composition of the high-speed steel tools were not varied except that a study was made of tool performance as affected by the addition of cobalt to the 18 per cent tungsten type of tool steel.

In most cases the limiting factor of machinability is tool failure, and machinability can best be measured in terms of the cutting speed permitting a definite tool life; that is, machinability is proportional to the cutting speed permitting a definite tool life, and it is upon this basis that the term is used in this report. From this it follows that those materials which under otherwise fixed conditions permit the longest cuts without regrinding of the tools are described as the most readily machinable or to have the highest degree of machinability.

With finishing cuts, close adherence to dimensions and the nature of the finish left on the work piece are probably as important factors as tool life. However, no very satisfactory method has yet been worked out for the evaluation of the appearance or type of finish produced by a cutting tool.[8] The method of test selected made possible a close adherence to the desired dimensions.

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B. S. Journal of Research, RP319

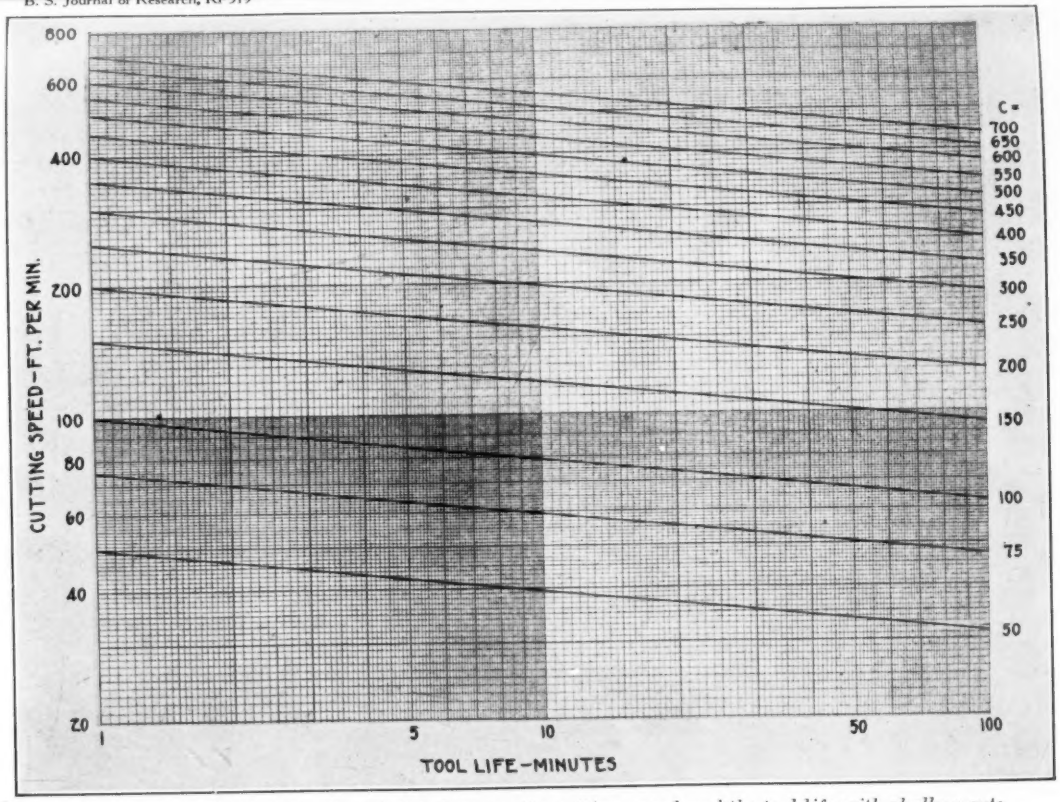


FIGURE 2.—*Chart giving the relation between the cutting speed and the tool life with shallow cuts*

This chart applies only to "dry" turning of steels with shallow cuts with high-speed steel tools. Lines drawn according to equation

$$VT^{1/10}=c,$$

in which $V$=cutting speed,
$T$=tool life,
$c$=constant.

## II. PREVIOUS INVESTIGATIONS

The results of previous lathe tests[9] made with high-speed steel tools with shallow cuts showed that with a constant feed and depth of cut there was a continuous increase in tool life as the cutting speed was decreased which could be represented approximately by the equation

$$VT^n = V_0 T_0^n = c \qquad (1)$$

in which

$V$ = cutting speed, feet per minute.
$T$ = tool life, minutes.
$T_0$ = 20 minutes.
$V_0$ = Taylor speed; that is, the speed which would give a tool life of 20 minutes.
$c$ = a constant for the metal (with specified heat treatment) which is being cut.
$n$ = a constant experimentally determined by varying $V$.

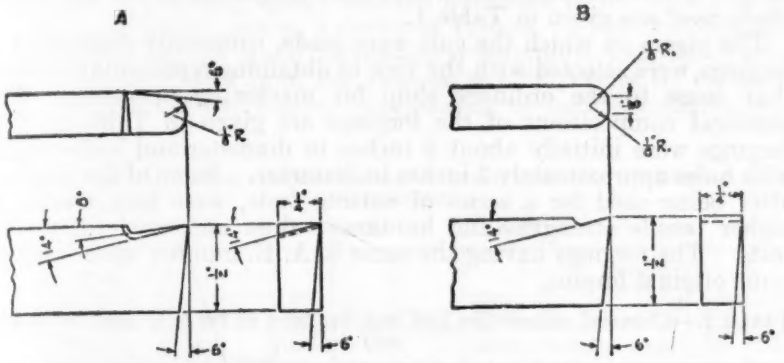


FIGURE 1.—*Dimensions and forms of the tools used in the lathe tests*
*A*, tool for roughing cuts; *B*, tool for shallow cuts.

The tests made at different cutting speeds with a feed of 0.015 inch per revolution and depths of cut of 0.010 and 0.020 inch showed that within a range of tool life of from 2 to 125 minutes, the experimental results could be closely represented by equation (1) with $n = 1/10$. This equation with $n = 1/10$ has therefore been used in the present report for all computations involving the relation between the cutting speed and tool life and gives results sufficiently accurate for all practical purposes except when extrapolating for very long tool life from tests of short duration.

Equation (1) with $n = 1/10$ was established with broadnose high-speed steel tools, illustrated in Figure 1 (*B*), in dry cutting 3½ per cent nickel steel forgings having tensile strengths between 80,000 to 100,000 lbs./in.$^2$. This equation is represented graphically by straight lines when log-arithmetic coordinates are used. The chart shown in Figure 2 for finishing cuts is of a convenient form for computing the life of tools at various speeds. Numerically the constant "$c$" is the cutting speed corresponding to a tool life of one minute.

[9] See footnote 7, p. 978.

## III. METHOD OF TEST

The method used for testing lathe tools with shallow cuts has been described in detail in a previous report.[10] With this method the test and indicating tools were set at equal depths in a special tool holder at the start of the test. The indicating tool began to cut when the wear on the test tool was from 0.001 to 0.002 inch, and this was considered as the point of failure of the test tool. In most cases it was found that the wear of 0.001 to 0.002 inch coincided with a complete breakdown of the tool comparable to that found with heavy cuts in rough turning.

From 6 to 10 tools were tested for each condition investigated and only average values of tool life were used for computation and comparison purposes.

The lathe tests with shallow cuts were made with high-sped steel tools of the broad-nose type, having dimensions and form shown in Figure 1 (*B*). A round nose tool (fig. 1 (*A*)) was used for the indicator. Chemical composition and heat treatment of the high-speed steels used are given in Table 1.

The pieces on which the cuts were made, commonly referred to as forgings, were selected with the view of obtaining representative steels that come to the ordinary shop for machining operations. The chemical compositions of the forgings are given in Table 2. The forgings were initially about 8 inches in diameter and hollow bored with holes approximately 3 inches in diameter. Some of the forgings, after being used for a series of cutting tests, were heat treated to higher tensile strengths and hardness values and used for further tests. The forgings having the same S. A. E. number were from the same original forging.

TABLE 1.—*Chemical composition and heat treatment of the tools used in the lathe tests*

| Steel No. | Chemical composition | | | | | | | | | | Quenched from [1] | Tempered at [2] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Mn | P | S | Si | Cr | W | V | Co | Mo | | |
| | *Per ct.* | *Per ct.* | *Per ct.* | *Per ct.* | *Per ct.* | *Per ct.* | *Per ct.* | *Per ct.* | *Per ct.* | *Per ct.* | °F. | °F. |
| AA | 0.68 | 0.20 | 0.031 | 0.013 | 0.21 | 3.79 | 18.2 | 0.99 | ------ | ------ | 2,400 | 1,100 |
| BB | .70 | .30 | .030 | .031 | .14 | 3.68 | 17.6 | 1.18 | 4.5 | 0.05 | 2,450 | 1,100 |
| CC | .69 | .17 | ------ | ------ | .34 | 4.23 | 18.3 | 1.53 | 7.8 | .96 | 2,450 | 1,100 |
| Y | .79 | .42 | .030 | .005 | .15 | 4.57 | 21.5 | 1.47 | 11.7 | .61 | 2,450 | 1,100 |

[1] All tools were first annealed by heating for 2 to 3 hours at 1,600 to 1,650° F. and furnace cooled. They were preheated for 20 minutes at 1,600° F. and then held 1½ minutes in the high-temperature furnace at the temperature indicated.

[2] Tools were heated in the furnace to the temperature indicated, held 30 minutes, and air cooled.

TABLE 2.—*Chemical composition of the forgings cut in the lathe tests*

| Forging No. | S. A. E. No. | Chemical composition [a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | C | Mn | P | S | Si | Cr | V | Ni | Mo |
| | | *Per cent* | *Per cent* | *Per cent* | *Per cent* | *Per cent* | *Per cent* | *Per cent* | *Per cent* | *Per cent* |
| 46 | 6140 | 0.39 | 0.71 | 0.019 | 0.029 | 0.20 | 0.95 | 0.17 | ------ | ------ |
| 47 | 4140 | .39 | .86 | .020 | .023 | .22 | .86 | ------ | ------ | 0.17 |
| 48 | 3435 | .39 | .59 | .017 | .019 | .26 | .76 | ------ | 2.96 | ------ |
| 49 | 3140 | .37 | .64 | .021 | .024 | .20 | .50 | ------ | 1.26 | ------ |
| 50 | 2340 | .36 | .73 | .026 | .025 | .20 | ------ | ------ | 3.43 | ------ |
| 51 | 1040 | .42 | .65 | .020 | .015 | .19 | ------ | ------ | ------ | ------ |

[a] Chemical analysis data reported by the manufacturers.

[10] See footnote 7, p. 978.

The heat treatments and corresponding average mechanical properties of the forgings are given in Table 3. Average mechanical properties were determined from two or more specimens cut longitudinally from the forgings so as to represent the average properties of the metal removed during cutting. Likewise, the micrographs were made on sections representing the metal removed during the cutting tests.

The hardness of some of the forgings after heat treatment was above the range of what is considered commercially machinable with the present high-speed steel tools. This condition made possible a survey of the entire machinable range from the soft or annealed steel to the upper limit of the usual machinability range.

All cutting tests were made "dry" with a constant feed of 0.0115 inch per revolution, depth of cut of 0.010 inch and variable speed, depending upon the properties of the metal cut. The cutting speed was varied with the different steel forgings, but was kept constant for each series of tests on a given forging with given mechanical properties. In general, the cutting speeds selected were such as to give a tool life of from 10 to 30 minutes as is shown in Table 4. From the data thus obtained the cutting speed permitting a 20-minute tool life (Taylor speed) was computed from the average tool-life values by means of equation 1 with $n = 1/10$ or by extrapolating by using the chart shown in Figure 2.

TABLE 3.—*Heat treatment and average mechanical properties of the forgings cut in the lathe tests*

| Forging No.[2] | Heat treatment: Quenching[3] Temperature | Heat treatment: Quenching[3] Medium | Heat treatment: Tempering[4] Temperature | Heat treatment: Tempering[4] Time | Proportional limit | Yield point | Tensile strength | Elongation in 2 inches | Reduction of area | Rockwell hardness B | Rockwell hardness C | Shore hardness No. | Brinell hardness No. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | *1,000 lbs./in.²* | *1,000 lbs./in.²* | *1,000 lbs./in.²* | *Per cent* | *Per cent* | | | | |
| | *°F.* | | *°F.* | *Hours* | | | | | | | | | |
| CARBON STEEL S. A. E. 1040[1] | | | | | | | | | | | | | |
| 51 | 1,650 | Water | 500 | 6.5 | 69.0 | 84.7 | 123.6 | 17.8 | 55.5 | 100.5 | 20.6 | 37 | 241 |
| 51A | 1,650 | do | 800 | 4 | 64.0 | 76.0 | 111.8 | 20.5 | 57.3 | 96.0 | 15.2 | 36 | 229 |
| 51B | 1,650 | do | 1,100 | 4 | 52.5 | 60.5 | 95.7 | 31.3 | 64.2 | 90.0 | 9.5 | 25 | 184 |
| 51C | 1,650 | do | 1,300 | 4 | 47.0 | 54.0 | 87.5 | 31.5 | 57.8 | 87.0 | ------ | 27 | 167 |
| 51D | 1,650 | do | 1,550 | *4 | 47.5 | 48.5 | 78.0 | 34.0 | 53.5 | 81.5 | ------ | 26 | 149 |
| CHROMIUM-VANADIUM STEEL S. A. E. 6140[1] | | | | | | | | | | | | | |
| 46 | 1,650 | Oil | 500 | 3 | 98.5 | 114.0 | 145.4 | 15.0 | 55.8 | 106.5 | 30.1 | 50 | 300 |
| 46A | 1,650 | do | 850 | 4 | 98.0 | 110.0 | 135.5 | 15.0 | 52.3 | 105.0 | 26.4 | 41 | 290 |
| 46B | 1,650 | do | 1,100 | 4 | 87.0 | 90.0 | 114.3 | 20.5 | 60.8 | 100.0 | 21.2 | 38 | 230 |
| 46C | 1,650 | do | 1,350 | 4 | 55.0 | 61.5 | 96.0 | 30.8 | 60.8 | 92.0 | 10.0 | 31 | 192 |
| 46D | 1,650 | do | 1,550 | *4 | 42.5 | 49.8 | 90.4 | 29.5 | 53.5 | 89.0 | ------ | 28 | 168 |
| 46E | 1,625 | Water | 500 | 4 | 95.0 | 164.2 | 181.8 | 10.0 | 33.5 | 110.0 | 37.3 | 55 | 372 |

[1] Refer to Table 2 for chemical composition.

[2] Forgings Nos. 46, 47, 48, 49, 50, and 51 were first annealed by heating at 1,400° to 1,420° F. and cooled in furnace to 1,100° to 1,200° F. and then cooled in air to room temperature. These forgings were approximately 8 inches in diameter and hollow bored with holes 3 inches in diameter. Forging No. 46A had the same chemical composition and heat treatment as No. 46 except for the retempering treatment, 46B has the same heat treatment as 46A except for the retempering treatment, etc. This procedure was followed in numbering and heat treating the forgings used in the tests with shallow cuts. The forgings at the time of the second quenching treatment were smaller in diameter than at the time of first quenching treatment. This change in size accounts for the higher tensile strengths and hardness obtained in the latter case.

[3] Forgings were heated with the furnace to the hardening temperatures in 3 to 4½ hours, held at temperatures from 1½ to 3½ hours and cooled as indicated.

[4] Forgings were cooled in air from the tempering temperatures except those marked with an asterisk (*), which were cooled slowly in the furnace.

TABLE 3.—*Heat treatment and average mechanical properties of the forgings cut in the lathe tests*—Continued

CHROMIUM-MOLYBDENUM STEEL S. A. E. 4140 [1]

| Forging No. | Heat treatment | | | | Proportional limit | Yield point | Tensile strength | Elongation in 2 inches | Reduction of area | Rockwell hardness | | Shore hardness No. | Brinell hardness No. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Quenching | | Tempering | | | | | | | B | C | | |
| | Temperature | Medium | Temperature | Time | | | | | | | | | |
| | °F. | | °F. | Hours | 1,000 lbs./in.² | 1,000 lbs./in.² | 1,000 lbs./in.² | Per cent | Per cent | | | | |
| 47 | 1,625 | Water | 700 | 4 | 79.0 | 121.5 | 137.2 | 18.0 | 59.4 | 104.5 | 27.8 | 41 | 287 |
| 47A | 1,625 | do | 900 | 4 | 83.0 | 96.2 | 120.7 | 18.5 | 59.5 | 102.0 | 23.9 | 38 | 255 |
| 47B | 1,625 | do | 1,100 | 4 | 70.0 | 76.6 | 108.8 | 26.5 | 63.1 | 95.5 | 15.2 | 31 | 204 |
| 47C | 1,625 | do | 1,350 | 4 | 48.0 | 54.3 | 93.7 | 30.0 | 60.7 | 90.0 | 7.9 | 30 | 179 |
| 47D | 1,625 | do | 1,550 | ¼ | 35.0 | 41.0 | 89.0 | 28.0 | 43.7 | 87.5 | ------ | 26 | 166 |
| 47E | 1,625 | do | 500 | 4 | 127.0 | 165.8 | 210.9 | 6.5 | 31.8 | 112.5 | 42.5 | 59 | 388 |
| 47F | 1,625 | do | 750 | 4 | 110.0 | 143.8 | 163.3 | 13.8 | 47.8 | 108.5 | 33.8 | 53 | 321 |
| NICKEL-CHROMIUM STEEL S. A. E. 3435 [1] | | | | | | | | | | | | | |
| 48 | 1,540 | Oil | 700 | 4 | 142.0 | 195.0 | 215.5 | 9.8 | 37.0 | 114.5 | 42.7 | 61 | 429 |
| 48A | 1,540 | do | 900 | 4 | 112.5 | 130.5 | 149.0 | 19.0 | 52.9 | 107.5 | 32.6 | 50 | 321 |
| 48C | 1,540 | do | 1,300 | 4 | 48.5 | 97.5 | 166.0 | 14.3 | 23.0 | 108.0 | 33.9 | 51 | 321 |
| 48D | 1,540 | do | 1,500 | ¼ | 65.0 | 70.0 | 109.5 | 24.5 | 55.0 | 97.0 | 15.5 | 32 | 204 |
| 48F | 1,500 | do | 700 | 4 | 171.5 | 188.2 | 207.0 | 7.3 | 33.5 | 113.5 | 42.5 | 61 | 415 |
| 48G | 1,500 | do | 800 | 4 | 160.0 | 166.5 | 183.1 | 12.0 | 42.5 | 111.5 | 39.5 | 55 | 388 |
| 48H | 1,500 | do | 1,050 | 4 | 113.5 | 118.7 | 135.0 | 16.7 | 55.9 | 104.5 | 27.4 | 47 | 269 |
| NICKEL-CHROMIUM STEEL S. A. E. 3140 [1] | | | | | | | | | | | | | |
| 49 | 1,500 | Water | 700 | 4 | 81.0 | 85.3 | 120.6 | 21.7 | 58.7 | 101.5 | 23.3 | 41 | 257 |
| 49A | 1,500 | do | 900 | 4 | 75.0 | 76.7 | 109.3 | 26.0 | 62.6 | 97.0 | 17.0 | 37 | 217 |
| 49B | 1,500 | do | 1,200 | 4 | 56.0 | 62.8 | 92.5 | 29.0 | 68.3 | 90.0 | 9.1 | 30 | 176 |
| 49C | 1,500 | do | 1,325 | 4 | 60.0 | 61.0 | 94.7 | 31.7 | 64.0 | 90.5 | ------ | 28 | 178 |
| 49D | 1,500 | do | 1,500 | ¼ | 55.0 | 56.0 | 89.0 | 31.2 | 55.0 | 87.5 | ------ | 27 | 170 |
| 49E | 1,500 | do | 500 | 4 | 112.5 | 184.5 | 202.8 | 7.8 | 24.6 | 113.0 | 42.2 | 58 | 406 |
| 49F | 1,500 | do | 750 | 4 | 96.7 | 122.7 | 140.0 | 14.4 | 50.7 | 104.5 | 28.0 | 45 | 282 |
| NICKEL STEEL S. A. E. 2340 [1] | | | | | | | | | | | | | |
| 50 | 1,525 | Oil | 500 | 3 | 71.5 | 125.5 | 150.0 | 13.2 | 45.3 | 106.5 | 30.7 | 42 | 302 |
| 50A | 1,525 | do | 800 | 4 | 89.5 | 94.0 | 121.5 | 22.0 | 56.4 | 101.5 | 24.7 | 39 | 255 |
| 50B | 1,525 | do | 1,100 | 4 | 72.0 | 78.3 | 105.8 | 27.3 | 64.8 | 97.5 | 18.5 | 34 | 215 |
| 50C | 1,525 | do | 1,325 | 4 | 49.0 | 66.8 | 116.0 | 22.5 | 42.7 | 98.0 | 18.3 | 34 | 226 |
| 50D | 1,525 | do | 1,500 | ¼ | 61.7 | 63.5 | 101.6 | 24.8 | 44.0 | 93.5 | 12.9 | 28 | 183 |
| 50E | 1,500 | do | 500 | 4 | 106.0 | 136.1 | 178.8 | 6.5 | 28.8 | 110.0 | 36.5 | 52 | 363 |

[1] Refer to Table 2 for chemical composition.

## IV. RESULTS OF CUTTING TESTS

The machining properties of a steel forging are recognized as being affected by (1) its chemical composition, (2) heat treatment after working, and (3) quality of the metal cut. The term "quality" refers to those details of composition and constitution not defined by ordinary chemical analysis or by a statement of the heat treatment, but which, nevertheless, may play a part in making a metal well suited for a particular service. So-called high quality for one service may be inferior for a different service; the term is general in nature as used in this report. It simply implies recognition of the fact that there are other factors beside chemical composition and heat treatment which may contribute to the final properties of the metal.

In the following experiments most attention was given to the first variable, chemical composition. However, the data throw some light upon the second variable, heat treatment; the quality of the metal was assumed to be practically constant in so far as each type composition was concerned.

As is shown in Table 2, most of the forgings selected were alloy steels which contained approximately 0.4 per cent carbon. A plain carbon steel of similar carbon content was included so that comparisons could be made of the effects on tool performance or machinability of chromium, molybdenum, vanadium, and nickel, either alone or in combination.

The alloy steels were supplied through the courtesy of the Central Alloy Steel Corporation, now the Central Alloy Division of the Republic Steel Corporation, Massillon, Ohio. The plain carbon steel forging was contributed by the Illinois Steel Co., Chicago, Ill.

It is not practicable to select a single cutting speed with a fixed feed and depth of cut for tool testing on steel forgings with tensile strengths varying over the wide range of 75,000 to 220,000 lbs/in.[2] For example, if a cutting speed was selected to give a tool life of 10 to 30 minutes on a forging heat treated to give a tensile strength of 90,000 lbs./in.[2] and then an attempt was made to use the same cutting condition on a forging of similar composition, but with a tensile strength of 200,000 lbs./in.[2], the result would be immediate tool failure. Similarly, if the cutting speed was selected to give the desired tool life on the forging with high strength, then the tool life on the forging of lower strength would be extremely long. As already shown, the relation between the cutting speed and tool life of high-speed steel tools, under fixed feed and depth of cut can be closely represented by an empirical equation, and this fact was used in selecting the speeds at which the tool tests were made.

The comparisons of the different steels cut may conveniently be made on the basis of equal tensile strengths and the Taylor speed, such a comparison being taken as a measure of machinability.

TABLE 4.—*Summary of lathe tests on different steels at 0.0115 inch per revolution feed and 0.010 inch depth of cut.*[1]

CARBON STEEL S. A. E. 1040

| Forging No. | Tensile strength | Cutting speed | Number of tests made | Average tool life | Taylor [2] speed | Forging No. | Tensile strength | Cutting speed | Number of tests made | Average tool life | Taylor [2] speed |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | *1,000 lbs. in.*[2] | *Ft./min.* | | *Minutes* | *Ft./min.* | | *1,000 lbs. in.*[2] | *Ft./min.* | | *Minutes* | *Ft./min.* |
| 51 | 123.6 | 180 | 8 | 10.5 | 169 | 51C | 87.5 | 310 | 8 | 19.9 | 310 |
| 51A | 111.8 | 200 | 8 | 7.4 | 181 | 51D | 78.0 | 325 | 8 | 12.0 | 310 |
| 51B | 95.7 | 250 | 7 | 17.1 | 246 | | | | | | |

CHROMIUM-VANADIUM STEEL S. A. E. 6140

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 46 | 145.4 | 200 | 8 | 13.4 | 192 | 46C | 96.0 | 290 | 8 | 32.3 | 304 |
| 46A | 135.5 | 230 | 8 | 14.8 | 223 | 46D | 90.4 | 315 | 8 | 18.5 | 313 |
| 46B | 114.3 | 280 | 7 | 14.1 | 270 | 46E | 181.8 | 120 | 7 | 26.0 | 123 |

[1] The lathe tests were made dry with high-speed tool steel numbered AA. Composition and heat treatment of tools are given in Table 1. Selected size and form of tool shown in Figure 1 (*B*).

[2] Computed from the average tool life by means of equation (1) of the text with $n=\frac{1}{10}$ or obtained from Figure 2.

TABLE 4.—*Summary of lathe tests on different steels at 0.0115 inch per revolution feed and 0.010 inch depth of cut*—Continued

CHROMIUM-MOLYBDENUM STEEL S. A. E. 4140

| Forging No. | Tensile strength | Cutting speed | Number of tests made | Average tool life | Taylor speed | Forging No. | Tensile strength | Cutting speed | Number of tests made | Average tool life | Taylor speed |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | *1,000 lbs./in.²* | *Ft./min.* | | *Minutes* | *Ft./min.* | | *1,000 lbs./in.²* | *Ft./min.* | | *Minutes* | *Ft./min.* |
| 47 | 137.2 | 180 | 8 | 41.2 | 194 | 47D | 89.0 | 340 | 8 | 24.4 | 347 |
| 47A | 120.7 | 230 | 7 | 24.1 | 234 | 47E | 210.9 | 60 | 8 | 19.1 | 60 |
| 47B | 108.8 | 320 | 8 | 11.2 | 302 | 47F | 163.3 | 150 | 8 | 8.1 | 137 |
| 47C | 93.7 | 310 | 8 | 26.0 | 318 | | | | | | |

NICKEL-CHROMIUM STEEL S. A. E. 3435

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 48 | 215.5 | 110 | 8 | 5.5 | 97 | 48D | 108.8 | 230 | 4 | 5.0 | 200 |
| 48A | 149.0 | 200 | 8 | 2.3 | 161 | 48F | 207.0 | 110 | 8 | 10.4 | 103 |
| 48C | 166.0 | 165 | 7 | 7.8 | 150 | 48G | 183.1 | 140 | 10 | 8.8 | 129 |
| 48D | 109.5 | 215 | 8 | 8.7 | 198 | 48H | 135.0 | 190 | 8 | 9.0 | 175 |

NICKEL-CHROMIUM STEEL S. A. E. 3140

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 49 | 120.6 | 200 | 7 | 20.2 | 200 | 49D | 89.0 | 330 | 8 | 19.6 | 329 |
| 49A | 109.3 | 250 | 7 | 14.6 | 242 | 49E | 202.8 | 110 | 8 | 17.9 | 109 |
| 49B | 92.5 | 320 | 10 | 21.9 | 323 | 49F | 140.0 | 180 | 8 | 16.4 | 177 |
| 49C | 94.7 | 320 | 8 | 16.8 | 314 | | | | | | |

NICKEL STEEL S. A. E. 2340

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 50 | 150.0 | 180 | 8 | 19.4 | 179 | 50D | 101.6 | 280 | 9 | 12.1 | 266 |
| 50A | 121.5 | 230 | 6 | 16.8 | 226 | 50D | 101.6 | 300 | 7 | 4.6 | 259 |
| 50B | 105.8 | 300 | 8 | 13.8 | 290 | 50E | 178.8 | 100 | 8 | 17.0 | 98 |
| 50C | 116.0 | 240 | 6 | 22.7 | 243 | | | | | | |

The results of the tests with shallow cuts are given in Table 4 and summarized in Figure 3. These data show that if machinability with shallow cuts is measured by the cutting speed permitting the tool to last a definite time, then measurable and consistent differences are observed in the machinability of the carbon and various alloy steels used in the experimental work. The fact, however, that some given steel permits a higher cutting speed than another steel for a selected tensile strength which is the same for both materials does not necessarily indicate that the two steels maintain the same relationship for another tensile strength. This is illustrated in Figure 3 in that, for the conditions of cutting under consideration, the chromium-molybdenum steel (S. A. E. 4140) had the best machinability of the entire group of steels at a tensile strength of 90,000 lbs./in.$^2$ At a tensile strength of about 110,000 lbs./in.$^2$ the chromium-vanadium steel (S. A. E. 6140) had the best machinability of the group and retained this superiority up to a tensile strength in the neighborhood of 175,000 to 180,000 lbs./in.$^2$ At this point the tensile strength-Taylor speed curve for the chromium-vanadium steel crosses the curves for the nickel-chromium steels (S. A. E. 3140 and 3435) and above this range the latter steels permit the higher cutting speeds.

As is also shown in Figure 3, the slopes of the tensile strength-Taylor speed curves vary for the different steels. The curves for any two compositions may cross and so reverse the order of superiority. In some cases the slopes were not very different and there was an

appreciable range in tensile strength at which, for all practical purposes, the cutting speeds were the same.

The plain carbon steel (S. A. E. 1040), within the range of tensile strengths obtained by heat treatments, was the most difficult of the group to machine other than the annealed nickel-chromium steel (S. A. E. 3435). This would indicate that the special alloying elements—nickel, chromium, molybdenum, and vanadium—either alone or in combination, when added to the plain carbon steel improve machinability from the standpoint of the cutting speed permitting a

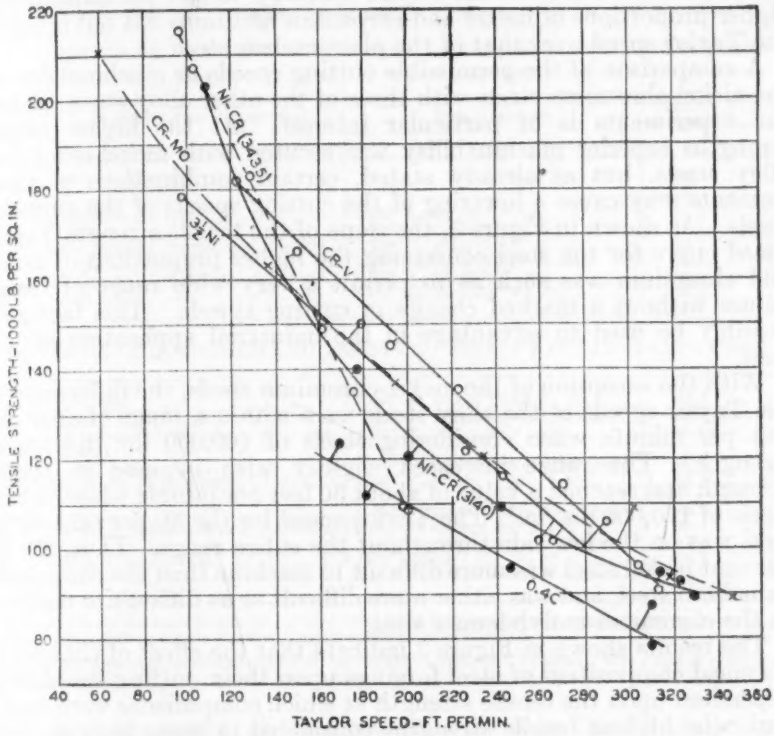


FIGURE 3.—*Relation of the Taylor speed to the tensile strength of the special steels cut in the lathe tests*

For details of chemical composition and heat treatment of steel cut, refer to Tables 2 and 3. The composition and heat treatment of high-speed steel tools No. AA used in the tests are given in Table 1. The lathe tests were made "dry" with the size and form of tool shown in Figure 1 (B), with 0.0115 inch per revolution feed and 0.010 inch depth of cut.

definite tool life with shallow cuts. However, the superiority in machinability of the alloy steels over the plain carbon type is not to be attributed solely to any single alloying element, but rather to the combined effects of the alloying elements present in any particular steel, considering carbon also as one of the alloying additions. This is evident from the fact that the same alloying elements which in one case increased the cutting speed, under other conditions, as, for example, when present in different relative proportions and requiring different heat treatments to give comparable tensile strengths, may be without any marked effect on the cutting speed.

This is illustrated by comparisons of the Taylor speeds of the nickel-chromium steels with that of the carbon steel at a tensile strength of 110,000 lbs./in.$^2$ The nickel-chromium steel containing 0.37 per cent carbon, 0.50 per cent chromium, and 1.26 per cent nickel had a Taylor speed of about 244 feet per minute, while the nickel-chromium steel containing 0.39 per cent carbon, 0.76 per cent chromium, and 2.96 per cent nickel showed the same Taylor speed as the plain 0.42 per cent carbon steel, namely, 198 feet per minute. Thus, at this particular tensile strength the addition of 0.5 per cent chromium and 1.26 per cent nickel increased the Taylor speed by 46 feet per minute, but higher proportions of nickel and chromium additions did not improve the Taylor speed over that of the plain carbon steel.

A comparison of the permissible cutting speeds or machinability of the nickel-chromium steels with those of the other alloy steels used in the experiments is of particular interest. At the higher tensile strengths superior machinability was secured with nickel-chromium alloy steels, but as already stated, certain combinations of these elements may cause a lowering of the cutting speeds of the annealed steels. As shown in Figure 3, the slope of the tensile strength-Taylor speed curve for the steel containing the higher proportions of nickel and chromium was such as to permit a very wide range of tensile values without a marked change in cutting speeds. This fact may possibly be used to advantage in the industrial application of this steel.

With the exception of the nickel-chromium steels, the differences in the Taylor speeds of the alloy steels were within a range of about 20 feet per minute when considering steels of 100,000 lbs./in.$^2$ tensile strength. The range increased slightly with increase in tensile strength and reached a value of about 30 feet per minute when cutting steels of 170,000 lbs./in.$^2$ The Taylor speed for the 3½ per cent nickel steel was on the low side throughout the entire range. Thus, the 3½ per cent nickel steel was more difficult to machine than the chromium-vanadium steel, and was either more difficult or as difficult to machine as the chromium-molybdenum steel.

The results shown in Figure 3 indicate that the effect of changes in chemical composition of steel forgings upon their cutting speeds was dependent upon the tensile strength at which comparisons were made. Since the highest tensile strengths considered in these tests are produced by quenching, with or without subsequent tempering, changes in chemical composition may act in opposite directions depending upon whether the steel cut is close to the fully hardened (martensitic) or the annealed (pearlitic) condition.

Elements which cause a lowering in the cutting speeds of the annealed steels may improve the cutting speeds when considering higher tensile strengths. Of the special elements that improved machinability of the different steels cut with shallow cuts, the most effective were the combinations of nickel and chromium or chromium and vanadium for the higher tensile strengths in the neighborhood of 180,000 lbs./in.,$^2$ while the combination of chromium and molybdenum was the most effective in the lower range of about 90,000 lbs./in.$^2$

The mechanical properties of the forgings, given in Table 3, and the cutting test results given in Table 4 permit comparisons to be made other than on the tensile strength-Taylor speed basis as given in the

text. The relative order of machinability of the different steel forgings when comparisons were made of the Brinell hardness numbers-Taylor speed agreed very closely with the order as given by the tensile strength-Taylor speed basis. This agreement might be expected. The order of machinability as given by the tensile strength-Taylor speed was changed when comparisons were made on the basis of the Rockwell hardness (B or C scale)-Taylor speed or Shore hardness-Taylor speed.

TABLE 5.—*Effect of method of heat treatment on the cutting speeds of steel forgings having equal tensile strengths*

| Test forging No. | Type composition (in per cent) | Heat treatment | Tensile strength | Taylor speed |
|---|---|---|---|---|
| | | | *1,000 lbs./in.²* | *ft./min.* |
| **COMPARISON OF DIFFERENT METHODS OF QUENCHING AND TEMPERING** | | | | |
| 50A | 0.36 carbon, 3.4 nickel | 1,525° F., oil; 800° F., air | 121.5 | 226 |
| 50C | do | 1,525° F., oil; 1,325° F., air | 116.0 | 243 |
| 49B | 0.37 carbon, 0.5 chromium, 1.3 nickel | 1,500° F., water; 1,200° F., air | 92.5 | 323 |
| 49C | do | 1,500° F., water; 1,325° F., air | 94.7 | 314 |
| 48X | 0.39 carbon, 0.8 chromium, 3.0 nickel | 1,500° F., oil; 850° F., air | [1] 166.0 | [2] 145 |
| 48C | do | 1,540° F., oil; 1,300° F., air | 166.0 | 150 |
| **COMPARISON OF QUENCHED AND TEMPERED STEELS WITH ANNEALED STEELS** | | | | |
| 51C | 0.42 carbon | 1,650° F., water; 1,300° F., air | 87.5 | 310 |
| 51D | do | 1,550° F., cooled slowly in furnace | 78.0 | 310 |
| 46C | 0.39 carbon, 1.0 chromium, 0.17 vanadium. | 1,650° F., oil; 1,350° F., air | 96.0 | 304 |
| 46D | do | 1,550° F., cooled slowly in furnace | 90.4 | 313 |
| 47C | 0.39 carbon, 0.9 chromium, 0.17 molybdenum. | 1,625° F., water; 1,350° F., air | 93.7 | 318 |
| 47D | do | 1,550° F., cooled slowly in furnace | 89.0 | 347 |
| 49C | 0.37 carbon, 0.5 chromium, 1.3 nickel | 1,500° F., water; 1,325° F., air | 94.7 | 314 |
| 49D | do | 1,500° F., cooled slowly in furnace | 89.0 | 329 |
| 50B | 0.36 carbon, 3.4 nickel | 1,525° F., oil; 1,100° F., air | 105.8 | 290 |
| 50D | do | 1,500° F., cooled slowly in furnace | 101.6 | 266 |

[1] Estimated from the known relation between tempering temperature and tensile strength.
[2] Value obtained from tensile strength, Taylor speed curve of Figure 3.

NOTE.—The lathe tests were made dry with high-speed tool steel AA (Table 1), with a feed of 0.0115 inch per revolution and 0.010 inch depth of cut. Selected form and size of tool shown in Figure 1(*B*).

The heat treatments of the forgings, as given in Table 3, show that the desired range of tensile properties were obtained by annealing, or by quenching, followed by tempering at different temperatures. The results also show that in some cases approximately equal tensile strengths were produced with a given forging by varying the methods of heat treatment.

The data given in Table 5 show that, in general, the cutting speeds were not appreciably affected by the method of heat treatment by which a given tensile strength was produced. The cutting speeds are slightly higher with the high tempering temperatures when comparisons are made of the different methods of quenching and tempering to produce approximately equal strengths. In two cases, namely, with the plain carbon steel (S. A. E. 1040) and 3½ per cent nickel steel (S. A. E. 2340) the better machinability was produced by the heat treatment consisting of quenching and subsequently tempering at a high temperature than with the annealing treatment used.

## V. TESTS WITH COBALT HIGH-SPEED STEEL TOOLS

High-speed steel tools containing considerable proportions of cobalt have been reported to give excellent performance when cutting hard metals and to have made possible the commercial machining of high manganese steel. In previous tests made at the National Bureau of Standards,[11] it was found that cobalt improved the performance of high-speed steel lathe tools, with both shallow and roughing cuts, but that the maximum benefits were obtained only with high-hardening temperatures.

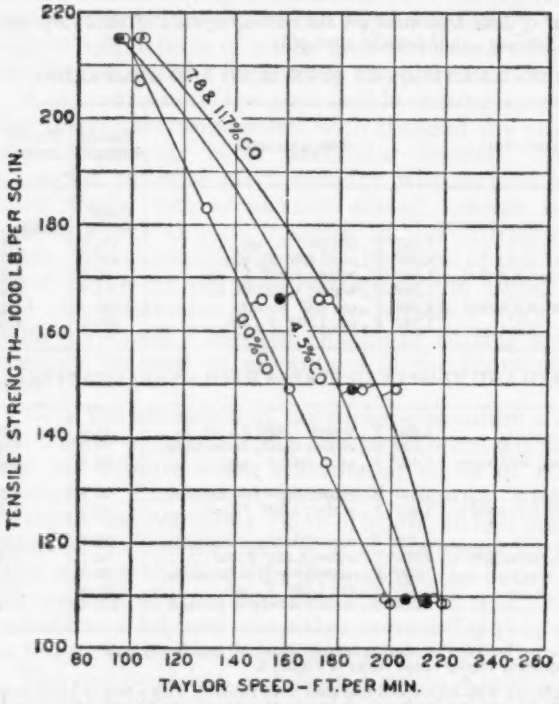


FIGURE 4.—*Relation of the Taylor speed to the tensile strength of the nickel-chromium (S. A. E. 3435) steel cut with high-speed steel tools containing different proportions of cobalt*

Chemical composition and heat treatment of the high-speed steel tools are given in Table 1. Chemical composition, heat treatment, and mechanical properties of the steel cut are given in Tables 2 and 3. The lathe tests were made "dry" with the size and form of tool shown in Figure 1 (*B*), with feed of 0.0115 inch per revolution and 0.010 inch depth of cut.

The proportionate gain in machinability from the addition of cobalt to high-speed steel tools was somewhat greater with rough turning than with shallow cuts, but increase in cobalt above about 5 per cent did not produce improvements commensurate with those resulting from additions of from 3.5 to 5 per cent together with high-hardening temperatures. These conclusions were made from experiments in cutting a 0.3 per cent carbon, 3½ per cent nickel steel forging heat treated to give a tensile strength of about 90,000 to 100,000 lbs./in.$^2$. Since high-speed steel tools containing high proportions of cobalt are claimed to be especially adapted to cutting hard materials, the tests with shallow cuts were extended to include the cutting of nickel chromium steel forgings (S. A. E. 3435) having tensile strengths between 100,000 and 220,000 lbs./in.$^2$.

The results of the cutting test carried out in the present investigation with high-speed steel tools, with and without cobalt, are summarized in Figure 4. The data show that lathe-tool performance with shallow cuts was improved by the additions of cobalt (together with higher hardening temperatures) to the customary 18 per cent

[11] See footnote 7, p. 978.

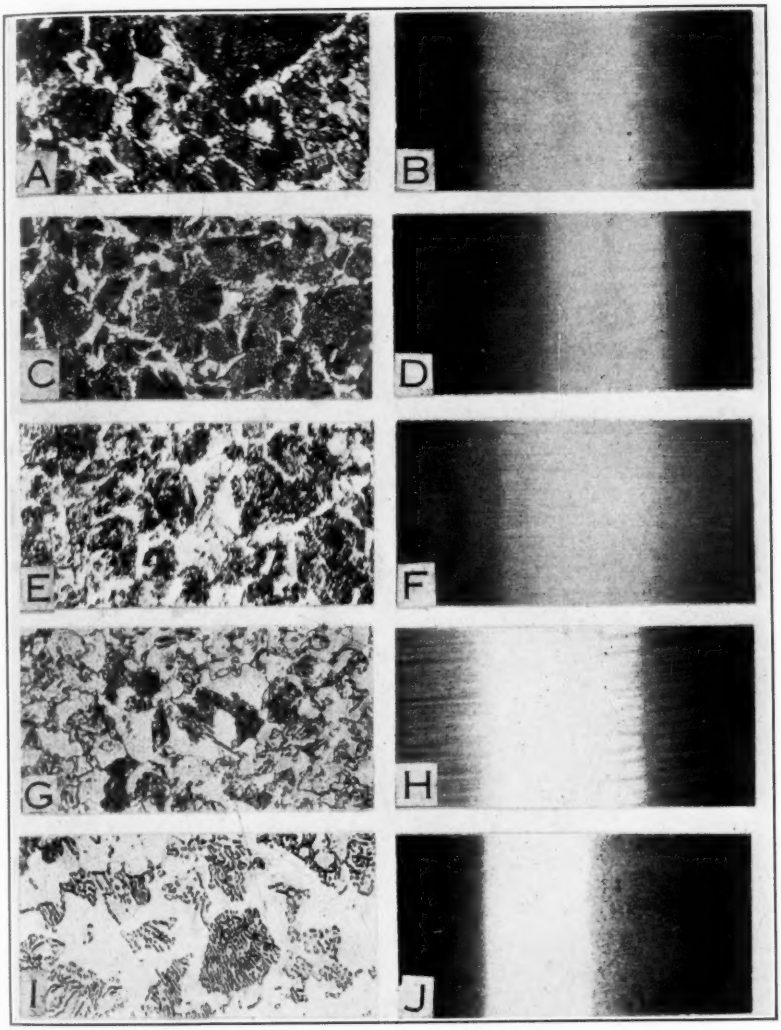


FIGURE 5.—*Microstructures and surface finishes of plain carbon (S. A. E. 1040) steel cut in the lathe tests*

For details of chemical composition and heat treatment of the forgings refer to Tables 2 and 3. The lathe tests were made "dry" with high-speed steel tools (AA) of size and form shown in Figure 1 (*B*), with 0.0115 inch per revolution feed and 0.010 inch depth of cut.

| Photomicrograph (×500) etched with 2 per cent nitric acid in alcohol | Surface finish (×1) | Forging No. | Tensile strength | Cutting speed | Taylor speed |
|---|---|---|---|---|---|
| | | | *1,000 lbs./in.²* | *Ft./min.* | *Ft./min.* |
| A | B | 51 | 123.6 | 180 | 169 |
| C | D | 51A | 111.8 | 200 | 181 |
| E | F | 51B | 95.7 | 250 | 246 |
| G | H | 51C | 87.5 | 310 | 310 |
| I | J | 51D | 78.0 | 325 | 310 |

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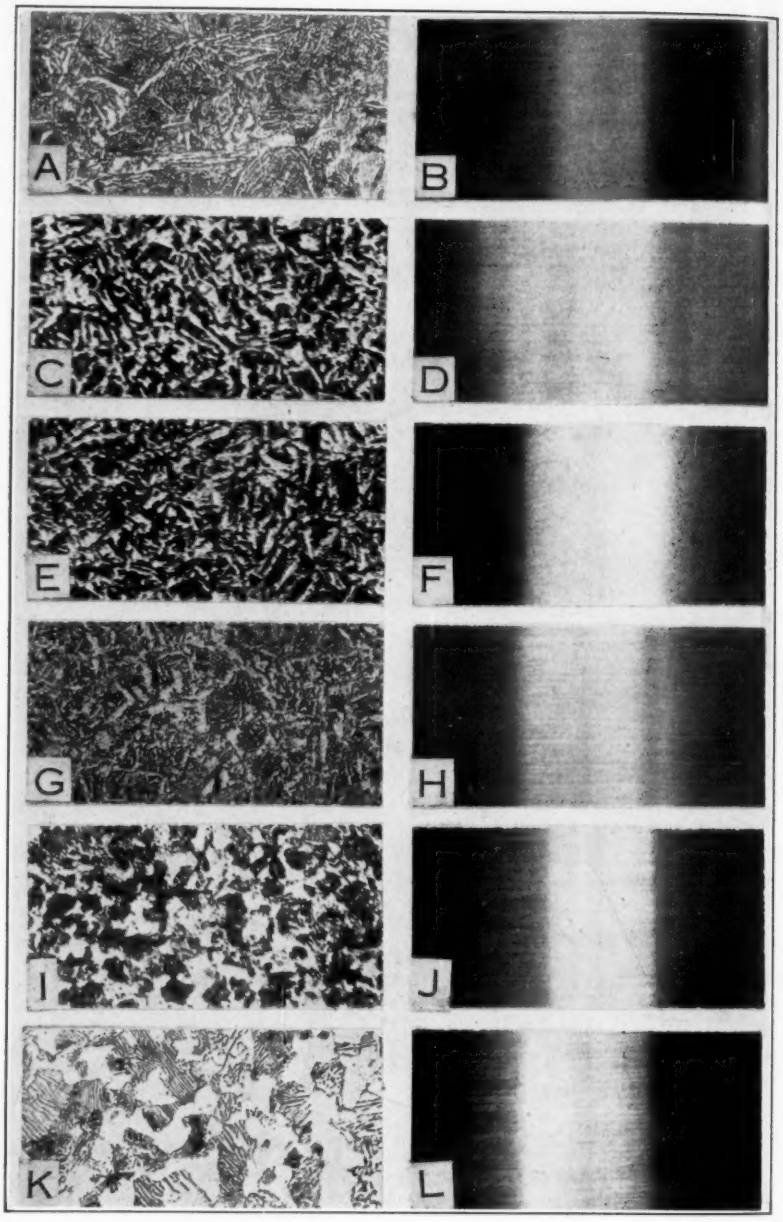


FIGURE 6.—*Microstructures and surface finishes of chromium-vanadium (S. A. E. 6140) steel cut in the lathe tests*

For details of chemical composition and heat treatment of the forgings refer to Tables 2 and 3. The lathe tests were made "dry" with, high-speed steel tools (AA) of size and form shown in Figure 1 (b), with 0.0115 inch per revolution feed and 0.010 inch depth of cut.

| Photomicrograph (×500) etched with 2 per cent nitric acid in alcohol | Surface finish (×1) | Forging No. | Tensile strength | Cutting speed | Taylor speed |
|---|---|---|---|---|---|
| | | | *1,000lbs./in.²* | *Ft./min.* | *Ft./min.* |
| A | B | 46E | 181.8 | 70 | 123 |
| C | D | 46 | 145.4 | 200 | 192 |
| E | F | 46A | 135.5 | 230 | 223 |
| G | H | 46B | 114.3 | 280 | 270 |
| I | J | 46C | 96.0 | 290 | 304 |
| K | L | 46D | 90.4 | 315 | 313 |

tungsten type of high-speed steel. Maximum gain in performance was obtained when cutting the forgings with tensile strengths up to about 170,000 lbs./in.$^2$; above this strength the gain in performance by increasing the cobalt additions was not so marked. Confirmation was also obtained of the previous test results, namely, that the increase in cobalt above about 5 per cent did not produce improvements of the same order as those resulting from 3.5 to 5 per cent, together with high-hardening temperatures.

## VI. MICROSTRUCTURES AND SURFACE FINISHES

Although most attention was given to tool life with shallow cuts in studying the machinability of the different forgings cut in the lathe tests, it was also recognized that the structure and appearance of the surface finish are important factors in finishing cuts and possibly may be considered as factors in any index to machinability.

Photographs were made of representative surface conditions while cutting with sharp tools for each series of cutting tests, and these photographs were later compared with the appearances as recorded by the observer during the machining operations. There was a fair agreement between the classification by the two methods. It was found that the photographs were a convenient but not an entirely satisfactory basis for making comparisons. All photographs were "natural size," and no attempts were made to show the surface conditions at greater magnifications.

The samples for microscopic examination were etched in 2 per cent nitric acid in alcohol and all micrographs are given at 500 magnifications. The microstructure shown in Figure 5 (*G*) corresponded to the best surface finish (shown at fig. 5 (*H*)) of the entire series of plain carbon steels (S. A. E. 1040) used in the experiments with shallow cuts. The resulting surface was fairly smooth and polished, with some tool marks; and while not so good as some of the surfaces produced on the different alloy steel forgings, it may be classed as satisfactory. The finishes as shown in Figure 5 (*B*), (*D*), (*F*), and (*J*) were dull, badly torn, with small bright particles embedded in the surface. None of the latter conditions were considered satisfactory so far as the appearance of the finish was concerned.

An interesting feature is shown by comparing the heat treatments, microstructures, tensile properties, finishes, and machinability of forgings 51C and 51D. Forging 51C, quenched from 1,650° F. in water and subsequently tempered at 1,300° F. and cooled in air shows some spheroidization or agglomeration of the cementite (fig. 5 (*G*)), satisfactory surface finish, 87,500 lbs./in.$^2$ tensile strength, and a Taylor speed of 310 feet per minute. Forging 51D, quenched from 1,650° F. in water and subsequently annealed at 1,550° F., slowly cooled in furnace, shows distinctly lamellar pearlite (fig. 5 (*I*) ), 81,500 lb./in.$^2$ tensile strength, and a Taylor speed of 310 feet per minute. Forging 51C, therefore, showed the best machinability both from the viewpoint of the cutting speed and appearance of the surface finish, provided comparisons of cutting speeds were made on the basis of equal tensile strengths.

For the cutting conditions investigated, the chromium-vanadium, chromium-molybdenum, nickel-chromium (3135), and 3½ per cent nickel-steel forgings were considered as producing surfaces of ap-

proximately equivalent smoothness, and were slightly superior to the nickel-chromium steel (3435). However, there were no very marked differences observed in the appearance of the surfaces of the forgings of the different alloy compositions, and all may be classified as satisfactory. Each type of alloy steel showed surfaces that were considered much superior to that of the plain carbon steel.

The characteristic finish of the different alloy steels may be described as smooth, medium to highly polished, with but little tearing and showing some tool marks.

The microstructures and surface finishes of all the alloy steel forgings with the varying heat treatments were examined, but no correlation between structure, surface finish, and machinability appeared possible. Figure 6 showing the microstructures and surface finishes of the chromium-vanadium forgings is representative of the results obtained with the alloy groups.

Vanick and Wickenden [12] have shown in some lathe tests of plain and alloy low-carbon steels of the carburizing type that for each steel and its particular heat treatment there was a critical range of volume removal rates within which a rough finish was obtained. By avoiding this critical range, smoothly finished surfaces could be obtained. It was found that cutting conditions leaving a rough surface could be changed to give a smooth finish by (1) either lowering, or preferably increasing the cutting speed until it is outside the critical range; (2) maintaining the speed, but changing the cut or feed; (3) sharpening the cutting angle of the tool and maintaining speed and shape of chip; (4) changing the hardness of the steel being cut; usually increasing it in order that a good finish is produced at an easily obtainable speed.

Rapatz [13] in a study of the surface conditions of plain-carbon and nickel-chromium steels of different strengths and hardness in some lathe turning tests found that higher tensile strengths, higher speeds, and greater depths of cut favored the production of smooth surfaces, assuming turning is performed with perfect tools. Yield point, elongation, and reduction of area were less important for obtaining smooth surfaces.

Although some of the surface finishes of the alloy steel forgings used in the present investigation were more highly polished and came nearer to being smooth than others, the differences observed in the general characteristics of the finishes were not large. The order in which the forgings were arranged in regard to the surface appearance under the conditions of test used, possibly might be different if the cutting conditions were changed.

## VII. SUMMARY AND CONCLUSIONS

1. The tests described in this report were made primarily as a study of high-speed steel tool performance with shallow cuts as affected by variations in the chemical composition and heat treatment of the steels cut. The study also included consideration of the surface finish of the various steel forgings, the microstructures of the metals cut, and also of the tool performance as affected by addi-

[12] J. S. Vanick and T. H. Wickenden, Smooth Finish Machining of Low-Carbon Plain and Alloy Steels, Trans. Am. Soc. Steel Treat., **11**, pp. 551; 1927.

[13] F. Rapatz, The Surface Conditions of Materials in Machining, Especially Turning, Archiv. fur Eisenhüttenwesen, **3**, p. 717; 1930.

tions of from 3.5 to 11.7 per cent cobalt to the 18 per cent tungsten type of high-speed steel.

2. The method used for testing lathe tools with shallow cuts was based upon the fact that when two tools are set at equal depths in one tool holder the second, or indicating tool, will not cut so long as the leading, or test tool, shows no wear. With this method of test, the indicating tool began to cut when the wear on the test tool was from 0.001 to 0.002 inch and this was considered as the point of failure of the test tool. In most cases, it was found that the wear of 0.001 to 0.002 inch coincided with a complete breakdown of the tool comparable to that found with heavy cuts in rough turning.

3. The lathe-cutting tests were made dry with high-speed steel tools of a selected size, form, composition, and heat treatment, with a fixed feed of 0.0115 inch per revolution, 0.010 inch depth of cut, and variable cutting speeds, depending upon the properties of the material cut.

4. The metals cut included a plain carbon and various alloy steel forgings heat treated to give tensile strengths between 75,000 and 220,000 lbs./in.[2]

5. The measure of machinability was the cutting speed permitting a definite tool life.

6. Measurable and consistent differences were observed in the machinability of the carbon and alloy steels used. The fact, however, that some given steel permits a higher cutting speed than another steel for some tensile strength which is the same for both materials does not necessarily indicate that the two steels maintain the same relationship for another tensile strength.

7. The 0.4 per cent plain carbon steel, within the range of tensile strengths obtained by heat treatments, was the most difficult to machine with shallow cuts other than an annealed nickel-chromium steel. The surface finishes of the carbon steel forgings were also inferior to those produced on the alloy steel forgings. However, with a particular heat treatment of the plain carbon steel, showing a microstructure of partially spheroidized or agglomerated cementite, a medium smooth and satisfactory finish was obtained with the cutting condition used. This same heat treatment also resulted in the best machinability of the group of carbon steels when comparisons were made on the basis of the cutting speeds at equal tensile strengths.

8. The superiority in cutting speeds of the alloy steels over the plain carbon type is not to be attributed solely to any single alloying element, but rather to the combined effects of the alloying elements present in any particular steel, considering carbon also as one of the alloying additions.

9. The results of the present tests with shallow cuts compared with previously reported tests with roughing cuts [14] show that the effect of changes in chemical composition of steel forgings upon their cutting speeds is dependent not only upon the tensile strength at which comparisons are made, but also upon the conditions of cutting. That is, steel forgings that show superior machinability with shallow cuts at some tensile strength do not necessarily show a similar superiority with roughing cuts.

10. Of the special elements that improved machinability of the different steels cut with shallow cuts, the most effective were the

[14] See footnote 4, p. 978.

combinations of nickel and chromium or chromium and vanadium for the higher tensile strenghths, in the neighborhood of 180,000 lbs./in.$^2$ and chromium and molybdenum in the lower range of tensile strengths, about 90,000 lbs./in.$^2$

11. In general, the cutting speeds were not appreciably affected by the method of heat treatment by which a given tensile strength was produced. The cutting speeds were slightly higher with the higher tempering temperature when comparisons were made of different methods of quenching and tempering to produce approximately equal tensile strengths. In two steels, namely, with the plain carbon steel and 3½ per cent nickel steel, the better machinability was produced by the heat treatment consisting of quenching and subsequently tempering at a high temperature than with the annealing treatments used.

12. Lathe-tool performance with shallow cuts was improved by the additions of cobalt (together with higher hardening temperatures) to the customary 18 per cent tungsten type of high-speed tool steel. The maximum gain in performance was shown when cutting the forgings with tensile strengths up to about 170,000 lbs./in.$^2$, but above this strength the gain in performance was not so marked.

13. Confirmation was also obtained of previous test results, namely, that the increase in cobalt above about 5 per cent did not produce improvements in tool performance of the same order as those resulting from 3½ to 5 per cent and higher hardening temperatures.

14. The differences observed in the surface finish of the different types of alloy steel forgings were not large and all were considered as being satisfactory and of about equivalent smoothness.

15. A correlation of the cutting speeds, tool life, surface finish, etc., shows that, with the test method used, the machinability of the carbon and different alloy steel forgings used in the experiments may be properly determined or measured by the cutting speed permitting the tool to last a definite time.

## VIII. ACKNOWLEDGMENTS

The writer acknowledges the assistance of E. C. Smith, chief metallurgical engineer, formerly of the Central Alloy Steel Corporation, Massillon, Ohio, for supplying the alloy steel forgings; and to S. Epstein, metallurgist, formerly of the Illinois Steel Co., South Chicago, Ill., for supplying the carbon steel forging used in the cutting tests.

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Washington, March 18, 1931.

# THE INDEX OF REFRACTION OF SOME SODA-LIMESILICA GLASSES AS A FUNCTION OF THE COMPOSITION

By C. A. Faick and A. N. Finn

ABSTRACT

Twenty-one soda-silica and twenty-one soda-lime-silica glasses were made in platinum and the index of refraction and chemical composition of each glass were determined. From the data obtained equations were derived and a diagram was prepared showing the relations between index of refraction and composition of these glasses.

The diagram makes it possible to predict with considerable accuracy (1) the index of refraction of any glass, in the range of compositions considered, from its composition and (2) the compositions of the various glasses which have the same index of refraction.

Some evidence is presented indicating that index of refraction of the soda-silica glasses may be a simple function of certain soda-silica compounds which may be present in glass.

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## I. INTRODUCTION

Although the relation between index of refraction and chemical composition of glass has been given considerable attention in the past, most of the work has been done on glass whose composition and heat treatment are not definitely known. Many of the previous investigators based their work on compositions computed from the batch, disregarding material dissolved from the pot. Others analyzed the glasses and almost invariably found small amounts of oxides whose presence was unintended and complicated any adequate analysis of the data. Tillotson[1] and Peddle,[2] for example, based their work on batch compositions. Turner,[3] however, analyzed his glasses; but they contained varying amounts of $Al_2O_3$, $Fe_2O_3$, and MgO, which confuse the issue when studying a 2 or 3 component system. Consequently, the results obtained by these investigators are not all that might be desired.

A diagram by Morey and Merwin showing the relations between composition and index of refraction of soda-lime-silica glasses has been published,[4] but the data on which these relations are based have not yet been presented.

[1] J. Ind. and Eng. Chem., **3**, p. 897; 1911; **4**, p. 246; 1912.
[2] J. Soc. Gl. Tech., **4**, 1920; **5**, 1921; **6**, 1922; **7**, 1923.
[3] J. Soc. Gl. Tech., **4**, 1920; **5**, 1921; **6**, 1922; **7**, 1923.
[4] Int. Crit. Tables, **2**, p. 102.

Finn and Thomson,[5] analyzing such data from the literature as were available for the purpose, obtained a series of equations for expressing the relation between index of refraction and composition. Since their analysis indicated that more satisfactory results might be obtained by further careful experimental study of the subject, it was decided that this work should be undertaken.

## II. OUTLINE OF THE WORK

In order properly to investigate the variation in index of refraction with changes in chemical composition, it was considered desirable to study first the 2-component system, soda-silica, and then to extend the work to the 3-component system, soda-lime-silica. The composition of the glasses varied from approximately 50 per cent each of soda and silica to 14 per cent soda-86 per cent silica in the 2-component system; in the 3-component system lime varied from approximately 3 to 15 per cent.

To obtain glasses containing only the two or three constituents under consideration would necessitate the reduction to a minimum of all impurities in the batch material and the prevention of contamination during melting. Consequently, only the best batch materials available were used. The soda and lime were introduced as sodium carbonate and calcium carbonate of reagent quality. The silica was prepared by pulverizing portions of a large, colorless, transparent quartz crystal.[6] The glasses were melted in a 25 ml platinum crucible to prevent contamination during melting, and were annealed at approximately their highest annealing temperature. Although the glasses were made from pure materials and melted in platinum, their compositions were subsequently determined by careful chemical analyses.

## III. MAKING THE GLASS

To produce the desired glasses a special platinum resistance furnace was constructed. The heating unit consisted of approximately 40 turns of 0.8 mm 80 per cent platinum-20 per cent rhodium wire wound on an alundum core of the following dimensions: Bore, 2 inches; wall, ⅜ inch; length, 12 inches. It was surrounded by about 1 inch of electrically sintered magnesia, the rest of the insulation being diatomaceous silica. The furnace was supported about 16 inches above the table to facilitate manipulations incident to melting the glass. The platinum crucible was handled by placing it in the end of a long refractory tube whose inside diameter was slightly less than the diameter of the crucible at the top. This "holder" when in place reached about halfway into the furnace and extended about 8 inches below it. It was so supported by a sliding-clamp arrangement that it could be quickly raised or lowered and swung clear of the furnace for purposes of filling and stirring. (See fig. 1.) A platinum and platinum-rhodium thermocouple for measuring temperature was placed inside the crucible-supporting tube, with its junction nearly touching

[5] J. Am. Cer. Soc., 8; No. 8, August, 1925.

[6] The significant impurities in the batch materials were found to be as follows: The sodium carbonate contained 0.002 per cent $SiO_2$, 0.006 per cent $R_2O_3$, 0.003 per cent MgO, and 0.013 per cent $K_2O$; the calcium carbonate contained 0.05 per cent MgO; the quartz contained 0.075 per cent nonvolatile residue (with HF and $H_2SO_4$).

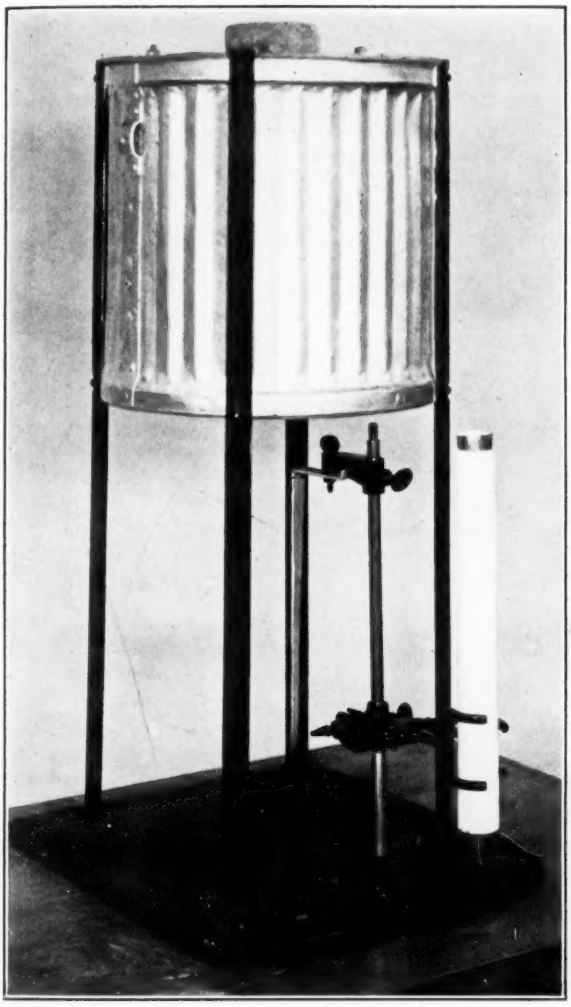

FIGURE 1.—*Melting furnace, showing the platinum crucible (in the refractory holder) in position for filling or stirring*

the crucible and its terminals extending out of the lower end. Extension leads connected the thermocouple to a potentiometer.

The filling was done at frequent intervals by lowering the crucible, swinging it clear of the furnace and adding small amounts of batch. Stirring was done with a platinum rod, the crucible being in the same position as for filling. After the glass was free from seeds and carefully stirred to eliminate striæ, it was poured from the crucible into an iron mold. This was done by removing the tube from its clamp and inverting it, thus obviating the necessity of handling the hot platinum crucible. The glass while still hot was transferred from the mold to a muffle furnace for annealing; the furnace being at a selected annealing temperature at the time of transfer. (See Table 1.)

The size of the samples of glass obtained was approximately 50 by 30 by 5 mm.

TABLE 1.—*Compositions, observed and calculated indices of refraction and differences between observed and calculated values of some soda-silica and soda-lime-silica glasses*

| Glass No. | Composition | | | Observed index | Computed index and differences | | | | Annealing temperature |
|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Na_2O$ | CaO | | A1 | A2 | B1 | B2 | |
| | *Per cent* | *Per cent* | *Per cent* | | | | | | °C. |
| 1 | 50.04 | 49.96 | | 1.5163 | 1.5159 | −0.0004 | 1.5158 | −0.0005 | 415 |
| 2 | 51.26 | 48.74 | | 1.5146 | 1.5152 | +.0006 | 1.5153 | +.0007 | 420 |
| 3 | 52.15 | 47.85 | | 1.5150 | 1.5148 | −.0002 | 1.5150 | .0000 | 420 |
| 4 | 54.14 | 45.86 | | 1.5137 | 1.5137 | .0000 | 1.5136 | −.0001 | 420 |
| 5 | 57.45 | 42.55 | | 1.5112 | 1.5116 | +.0004 | 1.5115 | +.0003 | 430 |
| 6 | 59.97 | 40.03 | | 1.5099 | 1.5101 | +.0002 | 1.5097 | −.0002 | 430 |
| 7 | 62.86 | 37.14 | | 1.5076 | 1.5076 | .0000 | 1.5075 | −.0001 | 440 |
| 8 | 63.06 | 36.94 | | 1.5075 | 1.5077 | +.0002 | 1.5073 | −.0002 | 440 |
| 9 | 65.30 | 34.70 | | 1.5055 | 1.5056 | +.0001 | 1.5055 | .0000 | 450 |
| 10 | 65.32 | 34.68 | | 1.5055 | 1.5056 | +.0001 | 1.5055 | .0000 | 480 |
| 11 | 67.14 | 32.86 | | 1.5042 | 1.5039 | −.0003 | 1.5041 | −.0001 | 500 |
| 12 | 69.65 | 30.35 | | 1.5021 | 1.5015 | −.0006 | 1.5022 | +.0001 | 515 |
| 13 | 70.21 | 29.79 | | 1.5014 | 1.5009 | −.0005 | 1.5017 | +.0003 | 525 |
| 14 | 70.44 | 29.56 | | 1.5015 | 1.5017 | +.0002 | 1.5015 | .0000 | 525 |
| 15 | 72.15 | 27.85 | | 1.4993 | 1.4992 | −.0001 | 1.5002 | +.0009 | 525 |
| 16 | 75.29 | 24.71 | | 1.4965 | 1.4955 | −.0010 | 1.4967 | +.0002 | 560 |
| 17 | 77.85 | 22.15 | | 1.4925 | 1.4923 | −.0002 | 1.4926 | +.0001 | 575 |
| 18 | 78.61 | 21.39 | | 1.4912 | 1.4915 | +.0003 | 1.4914 | +.0002 | 575 |
| 19 | 79.73 | 20.27 | | 1.4898 | 1.4900 | +.0002 | 1.4898 | .0000 | 575 |
| 20 | 83.00 | 17.00 | | 1.4851 | 1.4857 | +.0006 | 1.4846 | −.0005 | 600 |
| 21 | 86.41 | 13.59 | | 1.4790 | 1.4809 | +.0019 | 1.4794 | +.0004 | 600 |
| 22 | 52.65 | 43.05 | 4.30 | 1.5234 | 1.5233 | −.0001 | 1.5233 | −.0001 | 450 |
| 23 | 54.37 | 32.85 | 12.78 | 1.5391 | 1.5393 | +.0002 | 1.5394 | +.0003 | 530 |
| 24 | 56.20 | 34.00 | 9.80 | 1.5320 | 1.5322 | +.0002 | 1.5322 | +.0002 | 480 |
| 25 | 56.76 | 37.48 | 5.76 | 1.5238 | 1.5237 | −.0001 | 1.5236 | −.0002 | 470 |
| 26 | 58.41 | 38.54 | 3.05 | 1.5170 | 1.5172 | +.0002 | 1.5170 | .0000 | 480 |
| 27 | 60.32 | 24.50 | 15.18 | 1.5395 | 1.5404 | +.0009 | 1.5403 | +.0008 | 530 |
| 28 | 63.34 | 24.39 | 12.27 | 1.5320 | 1.5321 | +.0001 | 1.5321 | +.0001 | 525 |
| 29 | 64.14 | 21.22 | 14.64 | 1.5360 | 1.5361 | +.0001 | 1.5363 | +.0003 | 565 |
| 30 | 64.70 | 26.84 | 8.46 | 1.5232 | 1.5231 | −.0001 | 1.5233 | +.0001 | 525 |
| 31 | 65.71 | 28.79 | 5.50 | 1.5167 | 1.5163 | −.0004 | 1.5165 | −.0002 | 520 |
| 32 | 66.47 | 21.74 | 11.79 | 1.5288 | 1.5283 | −.0005 | 1.5286 | −.0002 | 565 |
| 33 | 67.30 | 29.43 | 3.27 | 1.5110 | 1.5103 | −.0007 | 1.5107 | −.0003 | 520 |
| 34 | 67.98 | 22.50 | 9.52 | 1.5230 | 1.5223 | −.0007 | 1.5228 | −.0002 | 565 |
| 35 | 70.50 | 23.00 | 6.50 | 1.5145 | 1.5136 | −.0009 | 1.5147 | +.0002 | 530 |
| 36 | 72.08 | 14.21 | 13.71 | 1.5265 | 1.5266 | +.0001 | 1.5268 | +.0003 | 580 |
| 37 | 72.61 | 24.24 | 3.15 | 1.5060 | 1.5047 | −.0013 | 1.5063 | +.0003 | 525 |
| 38 | 74.09 | 15.23 | 10.68 | 1.5182 | 1.5183 | +.0001 | 1.5181 | −.0001 | 545 |
| 39 | 74.81 | 12.14 | 13.05 | 1.5211 | 1.5222 | +.0011 | 1.5214 | +.0003 | 590 |
| 40 | 75.48 | 15.26 | 9.26 | 1.5138 | 1.5138 | .0000 | 1.5134 | −.0004 | 590 |
| 41 | 78.77 | 16.33 | 4.90 | 1.5003 | 1.5010 | +.0007 | 1.5002 | −.0001 | 545 |
| 42 | 80.59 | 16.17 | 3.24 | 1.4939 | 1.4955 | +.0016 | 1.4943 | +.0004 | 565 |

## IV. MEASUREMENT OF INDEX OF REFRACTION

The measurement of the indices of refraction presented difficulties because many of the glasses, especially those of low silica content, were very hygroscopic. In fact, most of them were so unstable that it was impossible to grind and polish Pulfrich slabs for index measurements. Consequently a different method was used. This was essentially an immersion method, whereby the index of refraction of a glass sample was matched by that of a liquid, and the index of the liquid then measured with an Abbe refractometer.

The apparatus for measuring index of refraction by this method is illustrated diagrammatically in Figure 2.

The immersion tank was equipped with two parallel plate glass windows to permit passage of light through the liquid, and was partially inclosed by a water chamber through which tap water was continually flowing. Water from the same source was also flowing through the refractometer to keep both the immersion liquid and the

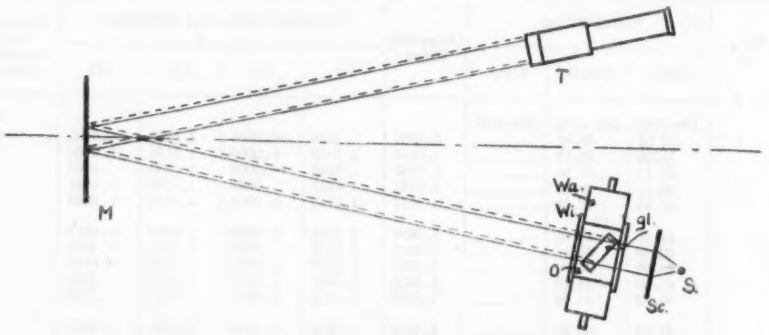


FIGURE 2.—*Diagrammatic sketch of immersion tank and optical system used in determining index of refraction*

The Abbe refractometer is not shown.
Key: *Wa*, water chamber; *Wi*, windows; *O*, immersion tank; *gl*, glass sample; *Sc*, object screen; *S*, source of light; *M*, mirror; *T*, telescope.

refractometer at practically the same temperature, and thus to eliminate any significant errors that might arise from temperature differences. The thermometers in the immersion liquid and in the water jacket of the refractometer prisms never differed from each other by more than 0.25°C.

The "object" (*Sc* in fig. 2) was a piece of fine-ground glass on which black cross lines were ruled. The source of light was a sodium flame. A telescope for observation, a mirror, a clip for suspension of the samples, and a stirrer to mix the component oils of the immersion liquid were also provided.

Two oils were used, Halowax oil ($N_d = 1.635$) and a light mineral oil ($N_d = 1.463$), making it possible to obtain a mixture having any index between 1.463 and 1.635.

In making index measurements the object screen (*Sc*) was illuminated by the sodium flame (*S*), the light after passing through the oil (*O*) and the sample (*gl*), being reflected by the mirror (*M*) to the telescope (*T*). The telescope was focused on the lines of the object screen. Then the oil and the glass were matched for index by

adding, with constant stirring, small amounts of one or the other of the oils to change slowly the index of the mixture until the mixed oils matched the glass. When not matched the lines of the object screen were distorted or broken up. Also, the lines visible through the sample shifted in position as the sample was rotated. When perfectly matched no distortion or shifting of the lines was observed, regardless of the position, motion, or shape of the sample. The index of refraction of the oil was then measured with the Abbe refractometer. Of course, it was necessary to have glass samples relatively free from striæ or the lines would be distorted by differences of index of refraction within the glass.

The reliability of this method was checked with several samples whose indices had previously been measured with a carefully calibrated Pulfrich refractometer. These indices were problably accurate to a few units in the fifth decimal place. The differences between the indices of refraction determined by the immersion and Pulfrich methods were less than two units in the fourth decimal place; these differences are within the limits of accuracy of the Abbe refractometer used.

## V. DATA OBTAINED AND RESULTS

Forty-two samples of glass suitable for index determinations were made. The compositions and indices of refraction of these glasses, and also the temperatures at which they were annealed, are given in Table 1.

If the indices of refraction of the soda-silica glasses are plotted against the silica or soda content of the glasses, an approximately smooth curve will be obtained. Although a curve of this kind can be represented by a number of different equations, it was found that satisfactory values for the refractivity of these glasses could be computed by the equation:

$$(N-1)=0.5054+0.000887\ A-0.000013543\ A^2 \qquad (1)$$

in which $N$ is the index of refraction for sodium light, $A$ is the percentage of silica, and the constants have been adjusted by the method of least squares.

Equation (1) can be arbitrarily divided into two others, one involving silica and the other involving soda; one group of such expressions is

$$(n_a-1)=0.005941\ A-0.000013543\ A^2 \qquad (2)$$
$$(n_b-1)=0.005054\ B \qquad (3)$$

in which $A$ and $B$ represent the percentages of silica and soda, respectively, and $n_a$ and $n_b$ represent their contributions to the index of refraction of the glass as computed for the silica and soda content from equations (2) and (3). Consequently, then

$$(N-1)=(n_a-1)+(n_b-1) \qquad (4)$$

gives the refractivity for the 2-component system.

For convenience "$n$" will be called a "partial index" of the glass, and when written with a subscript, such as $n_a$, the subscript will indicate the particular oxide in the glass to which the corresponding

capital letter refers. Regarding the derivation of equations (2) and (3), it is obvious that the effect of soda on the index of the glasses was assumed to be a linear function and all the curvature expressed by the last term in equation (1) was attributed to the silica.

If, now, we assume that the partial substitution of lime for soda in the soda-silica glasses does not affect the silica equation (2), then equations (2) and (3) can be used to compute the partial indices for the silica and soda in the glasses containing lime and the differences between the sum of these partial indices and the observed index of the lime glasses should yield data from which an expression for the partial index of lime can be computed. Proceeding on this assumption, the equation for the partial index of lime ($C$) is found to be

$$(n_c-1)=0.00707\ C \tag{5}$$

Hence, for the soda-lime-silica glasses

$$(N-1)=(n_a-1)+(n_b-1)+(n_c-1) \tag{6}$$

may be used for computing the refractivities.

The results obtained by equation (6) for all the glasses considered in this report are given in column A1, Table 1. The differences between the observed and computed values are given in column A2.

A consideration of the deviations (column A2, Table 1) for glasses 1 to 21, which are listed in the order of their increasing silica content, suggests a decided tendency toward systematic variations; this might merely indicate that equation (1) is not exactly of the best type to express properly the relations between composition and index of refraction, but several other expressions (some involving fractional exponents and others including terms in the second power of $N$ and the cross product of $N$ and $A$) were tried with quite similar results. The explanation of this systematic behavior of the residuals is apparent when the soda-silica data are carefully plotted on a large scale. It then becomes evident that the index of refraction of the soda-silica glasses does not change with composition in a manner such as to form a continuous curve like the values computed by (1), but from the data presented it seems that a broken curve made up of segments of three straight lines will more accurately express the relations.

These straight lines apparently intersect at points corresponding to 59.5 and 73.75 per cent silica and these percentages correspond quite closely to the silica content of $2Na_2O.3SiO_2$ and $Na_2O.3SiO_2$. This raises the question as to whether the changes in index with composition of the soda-silica glasses can be accurately represented by a smooth curve, as is ordinarily believed, or whether the index changes in a simpler (linear) manner which is directly related to certain molecular combinations which may be present in the glass.

Apparently this straight-line hypothesis can be applied to that part of the 3-component system discussed in this report, for the index of refraction of the soda-lime-silica glasses can also be more accurately expressed by straight-line equations. The general equation for the soda-silica and soda-lime, silica glasses is:

$$(N-1)=aA+bB+cC \tag{7}$$

in which $A$, $B$, and $C$ represent the percentages of silica, soda, and lime as before, and $a$, $b$, and $c$ are empirical constants having the following values in the indicated silica ranges:

| Silica range (in per cent) | $a$ | $b$ | $c$ |
|---|---|---|---|
| 50 ? to 59.5 | 0.004836 | 0.005491 | 0.007521 |
| 59.5 to 73.75 | .004785 | .005568 | .007598 |
| 73.75 to 100 | .004584 | .006127 | .007977 |

The 50 per cent limit for silica is subject to question, because the indicated constants ($a$, $b$, $c$) for the silica range 50 to 59.5 per cent may apply to glasses containing less than 50 per cent silica. No glasses containing less than 50 per cent silica were made. The limiting silica value of 73.75 per cent applies only to the soda-silica glasses. For lime glasses it gradually changes, as the lime is increased, to approximately 71 per cent silica when the lime content reaches 16 per cent. The limiting silica value in this case is indicated by the line $bb'$ in Figure 3.

The division lines between two adjacent groups were located by solving the corresponding equations simultaneously for the points of intersection of constant index lines. It will be observed that the boundary, $aa'$, between the first and second groups follows a constant silica line while $bb'$ between the second and third deviates toward lower silica values as the percentage of lime increases.

The results obtained by the proper substitutions in equation (7) are given in columns B1 and B2 of Table 1.

Comparing the deviations in columns A2 and B2 (Table 1), it can be seen that those in B2 are appreciably smaller than those in A2 and also that the tendency to systematic variation is less evident in B2 than in A2.[7]

If equations (6) and (7) are used to calculate the compositions of glasses having the same index of refraction, and these compositions plotted on a triordinate graph, lines of equal index of refraction are readily located. This was done, and the resulting lines for equal index are shown in Figure 3. The "dash" lines in Figure 3 are the lines of equal index of refraction of the soda-lime-silica glasses computed from equation (6). The dotted lines are the equal-index lines determined by Morey and Merwin,[8] and the solid lines are those derived from equation (7).

It becomes evident, after considering Figure 3, that there will be an infinite number of glasses containing only soda, lime, and silica that have the same index of refraction for sodium light. For example, the composition of a glass having an index of 1.51 may vary from 40 per cent $Na_2O$ : 60 per cent $SiO_2$ to approximately 11 per cent $Na_2O$ : 10 per cent CaO : 79 per cent $SiO_2$, provided the changes in composition follow the 1.51 index line. Furthermore, the index of a glass whose composition lies at a point between two index lines may be readily computed from the distances which separate the point from the adjacent lines.

[7] These systematic variations can be more readily detected by plotting the differences at their corresponding points on a $Na_2O$–CaO–$SiO_2$ diagram.
[8] See footnote 4, p. 993.

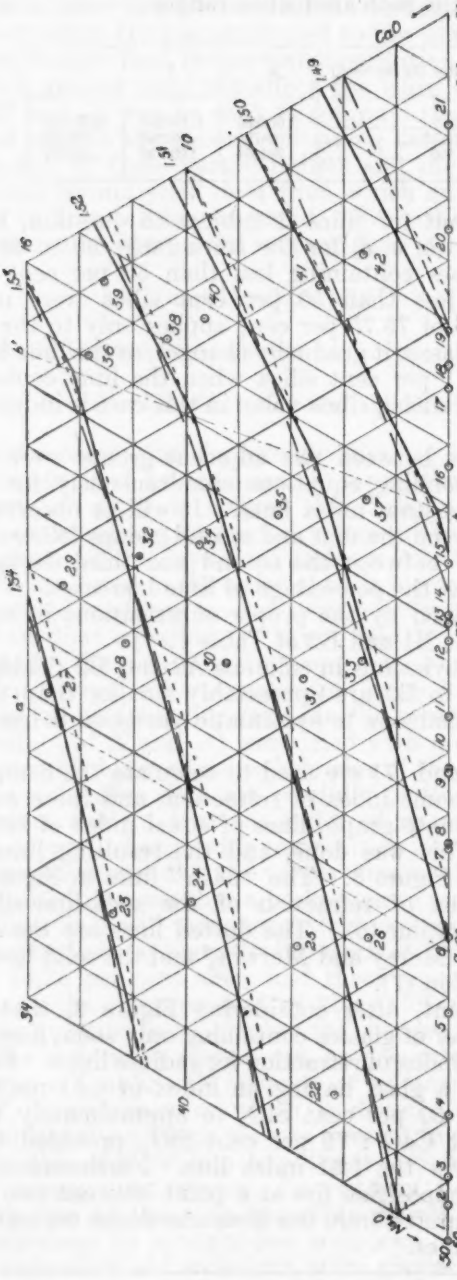


FIGURE 3.—*Diagram showing relation between composition and index of refraction of some soda-lime-silica glasses*

The "dash" lines were computed from equation (6), the solid lines from equation (7), and the dotted lines are reproduced from diagram by Morey and Merwin.

Although the equations given above can be used to compute the indices of refraction of the glasses considered, one must bear in mind the fact that the equations are wholly empirical and the division into forms involving partial indices is arbitrary.

## VI. DISCUSSION

An opinion of the reliability of the data in Table 1 and of the curves in Figure 3 can be formed only when one considers the probable accuracy of the chemical analyses and the index measurements.

The analyses of the glasses were made by F. W. Glaze, to whom credit is due for very careful and consistent work. His work was simplified by the fact that the glasses were made from very pure batch materials and were melted in platinum; consequently they did not contain more than traces of oxides other than the two or three under consideration.

Silica was determined by the ordinary fusion with sodium carbonate and double dehydration, followed by the addition of a small amount of alumina to collect residual silica with the ammonia precipitate. Appropriate blank determinations were made.

Soda was determined by either the J. L. Smith method, the zinc-uranyl acetate method, or both.

The first 15 glasses were analyzed in duplicate. The average difference between the duplicate determinations of silica was 0.07 per cent, the maximum being 0.16 per cent; the corresponding values for soda were 0.09 and 0.17 per cent.

In general, the lime glasses were not analyzed in duplicate nor were direct determinations of soda made; but for occasional checks, some determinations including soda were repeated, and the percentages of silica and soda as determined varied approximately as stated above while the average difference between the lime determinations was 0.03 per cent, the maximum being 0.09 per cent.

In all cases of complete analysis, the analyzed composition of the glass was adjusted to 100 per cent before the percentages were used in computing indices.

The reported index of refraction of the glasses is an average of three or more determinations on the same sample. Since a few striæ were present in some of these glasses, it is not certain that the accuracy of $\pm 0.0002$, which has been mentioned as obtainable in the method of measurement, was reached in all cases. It is thought, however, that the maximum error is not more than $\pm 0.0005$.

It has been shown [9] that the index of refraction (and also density) of a given glass may be materially changed by the temperature at which the glass is annealed; for instance, the index of refraction of a soda-lime glass similar to No. 39 (Table 1) will increase 0.000032 for each degree the effective annealing temperature is decreased in the range 570° to 500° C.; hence, the index of No. 39 may be made to change from 1.5211 to 1.5232 by proper heat treatment. Such changes in index (and density) are probably brought about by changes in the physicochemical constitution or equilibrium of the component constituents of the glass. Since equilibrium is attained much more quickly at higher than at lower temperatures, an effort was made to

[9] Tool and Hill, Trans. Soc. Glass Tech., **9**, p. 196; 1925. Annual Report of Director of the Bureau of Standards, p. 25; June 30, 1929. Also, Tool, Tilton, and Hill, J. Opt. Soc. Am. and Rev. Sci. Inst., **17**, p. 490; 1928.

anneal all of the experimental glasses at high temperatures in order to reduce to a minimum the time required for annealing.

In view of the foregoing statements it is not to be expected that soda-lime-silica glasses which have known compositions and are annealed at materially lower temperatures than those used (see Table 1) will have the indices indicated by Figure 3.

Although it is recognized that the chemical analyses and the indices of refraction of the glasses considered in this paper are not of the highest possible degree of accuracy, it is thought that the relations between index of refraction and composition shown in Figure 3 are more reliable than the individual determinations on which the relations are based because all the experimental data are included and there are no serious deviations between observed and computed values.

## VII. COMPARISON WITH OTHER DATA

The results obtained by Turner [10] were based on glasses containing small amounts of oxides of iron, aluminum, and magnesium. However, in the case of his data, if the amounts of iron and alumina are added to the silica, the magnesia is added to the lime, and all compositions adjusted to 100 per cent, and the resulting percentages substituted in equations (6) or (7) (or used in reading from fig. 3) the agreement between observed and computed indices is very good. In fact, the average variation between the observed indices of his 11 soda-lime-silica glasses and the values computed from their compositions by these equations is less than 0.0007, the maximum being 0.0019.

Peddle's results do not give satisfactory agreement when considered in the same way as Turner's; this may probably be explained by the fact that his reported compositions were computed from the batch and may vary materially from the composition of the finished glass.

## VIII. CONCLUSION

The significance of the work presented in this paper is threefold. First, it is possible to predict with considerable accuracy the index of refraction from the composition of any glass of the soda-lime-silica series in the range considered; second, the compositions of the numerous glasses of this series that have the same index of refraction can be predicted; and third, this work may serve as a check on the accuracy of chemical analysis of such glasses because, if a glass is annealed at a reasonably high temperature, its composition as determined by chemical analysis should fall on the line in Figure 3 representing its index of refraction.

There is also presented some evidence which suggests that the indices of refraction of the various soda-lime-silica glasses may be directly related to certain definite compositions (such as $2Na_20.3SiO_2$ and $Na_20.3SiO_2$) taken either singly or as simple mixtures, but more work must be done in order definitely to establish this point. This additional work is now under way.

WASHINGTON, March 30, 1931.

[10] J. Soc. Glass Tech., **4**, p. 111; 1920.

# VOLUME CHANGES IN BRICK MASONRY MATERIALS

By L. A. Palmer

ABSTRACT

Volume changes in bricks and mortars attending variations in moisture content and temperature have been studied. There were included in the study 21 cements (both Portland and masonry), 7 limes, and 8 makes of brick received from various sections of the United States. The shrinkage of mortars during hardening and the alternate expansion on wetting and shrinkage on drying occurring subsequent to hardening have been measured. Varying the moisture content produced far smaller volume changes in well-burned brick than in most of the mortars. Underburned brick expanded appreciably on wetting. It is indicated that differential volume changes between brick and mortar caused by variations in moisture content are apt to be greater than those produced by normal temperature variations. Volume changes in hardened mortars were least in the case of straight lime-sand mortars.

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## I. INTRODUCTION

### 1. PURPOSE AND SCOPE

It is reasonable to assume that the tendency of a mortar to remain bonded under any and all conditions is greater, the smaller its volume changes, provided, of course, that the masonry unit to which it adheres undergoes little or no expansion or contraction. In other words, by reducing to the lowest possible minimum the differential volume changes in unit masonry the life of the bond should be increased. Increasing the life of the bond between mortar and units should help in part at least to reduce water penetration through the masonry.

It is obvious that a volume change of a given magnitude would be more destructive in hardened than in plastic mortar. The latter occurrence would tend to interfere with the formation of a good bond, but the former would tend to destroy the bond, thereby producing partial or complete separation of the mortar and masonry unit. In vertical joints there would be a tendency for water to enter more readily after this has happened. However, it is reasonable to suppose that water might not penetrate so easily in load-bearing joints where pressure tends to keep mortar and units in intimate contact even when there is no adhesion of the one material to the other. This is in good agreement with what one may observe during a field study. Such observations make it very apparent that most of the excessive water penetration is between the mortar and units in vertical joints.

Sabin,[1] Pearson,[2] Schurecht and Pole,[3] Stradling,[4] White,[5] [6] and Davis and Troxell [7] have studied volume changes in masonry materials

[1] L. C. Sabin, Cement and Concrete, 2d ed., p. 106; 1907.
[2] J. C. Pearson, Shrinkage of Portland Cement Mortars and Its Importance in Stucco Construction, Proc. Am. Concrete Inst., **17**, p. 135; 1921.
[3] H. G. Schurecht and G. R. Pole, Effect of Water in Expanding Ceramic Bodies of Different Compositions, J. Am. Ceram. Soc., **12**, No. 9, pp. 596 to 604; 1929.
[4] R. E. Stradling, Department of Scientific and Industrial Research, Building Research Bulletin No. 3, Effects of Moisture Changes on Building Materials.
[5] A. H. White, Volume Changes in Portland Cement and Concrete, Proc. Am. Soc. for Testing Materials, **14**, p. 203; 1914.
[6] A. H. White, Destruction of Cement Mortars and Concrete through Expansion and Contraction, Proc. Am. Soc. for Testing Materials, **11**, p. 531; 1911.
[7] Raymond E. Davis and G. E. Troxell, Volumetric Changes in Portland Cement Mortars and Concretes, Proc. Am. Concrete Inst., **25**, pp. 210 to 260; 1929.

and emphasize either that expansion due to the taking up of moisture varies considerably among materials or that volume changes in mortars due to moisture absorption are greater than those due to thermal changes. In this work volume changes resulting from the absorption of water by brick and several types of mortars were specially studied, but attention was also given to thermal changes, including alternate freezing and thawing.

## 2. MATERIALS

One sand was used throughout in these tests. This was a fairly clean mortar sand, its screen analysis (made with United States standard sieves) being as follows:

| | Per cent |
|---|---|
| Passed No. 8 sieve, retained on No. 20 | 9. 2 |
| Passed No. 20 sieve, retained on No. 30 | 23. 0 |
| Passed No. 30 sieve, retained on No. 50 | 59. 2 |
| Passed No. 50 sieve, retained on No. 100 | 7. 7 |
| Passed No. 100 sieve | . 9 |
| Total | 100. 0 |

Eleven Portland cements were included in the study. These were representative of products of manufacturers in various parts of the United States. Two of these (Nos. 2 and 11) were white Portland cements. One of them (No. 5) was a quick hardening cement, this property being attributable more to fineness of particle size than to any other factor.

Seven limes were studied. Three (Nos. 1, 5, and 6) were high calcium limes. The others (Nos. 2, 3, 4, and 7) were dolomitic hydrates. No. 6 was the only quick (lump) lime used. These limes were representative of material produced in various sections of the United States.

There were 10 masonry cements. No. 1 was a mixture of hydrated lime and water-granulated blast-furnace slag. No. 2 was the same as Portland cement No. 11, but contained calcium stearate. No. 3 was a mixture of hydrated lime and Portland cement. No. 4 was a hydraulic lime. No. 5 was a Portland cement with paraffin added to give it water repellent properties. Nos. 6 and 9 were natural cements. No. 7 was a mixture of Portland cement, crushed limestone, and bentonite and No. 8 was a mixture of Portland and natural cements. No. 10 was a mixture of Portland cement and blast-furnace slag.

In the study of the effect of water-repellent substances on volume changes, calcium stearate alone was used. This substance is an insoluble soap, and is representative of a class of materials now being rather widely used.

Eight different manufacturers' products were used in the study of volume changes of brick. Two manufacturers included brick which they considered to be distinctly underburned and not representative of their marketable product. Both face and common brick made from clay or shale were included in the study. (Table 1.)

TABLE 1.—*Kinds of brick used*

| Brick No. | Range of total absorption (48 hours total immersion) | Molding process | Raw material |
|---|---|---|---|
| | *Per cent* | | |
| 1 | 11.5–17.5 | Dry-press | Mixture of surface clay and shale. |
| 2 | 5.2–10.7 | Stiff-mud, side cut | Shale. |
| 3 | 6.0–11.5 | do | Do. |
| 4 | 9.5–16 | Dry-press | Surface clay. |
| 5 | 4.2–9 | do | Fire clay. |
| 6 | 4.5–9.8 | Stiff-mud, side cut | Do. |
| 7 | 18.4–25.1 | Dry-press | Surface clay. |
| 8 | 19.4–25.6 | Soft mud | Do. |

## II. TEST PROCEDURE

### 1. PREPARATION OF TEST SPECIMENS

#### (a) MORTAR SPECIMENS

(1) PROPORTIONS OF DRY INGREDIENTS.—Except in the case of lime No. 6, the amounts of dry ingredients were proportioned on a volume basis. At the time of proportioning the weight as well as the volume of each dry ingredient was obtained.

The weight of the hydrated high calcium lime in the mortar composed of 1 volume of hydrated lime and 3 volumes of sand (1:3 mortars) was nearly one-seventh that of the sand for both limes. A 1:3 mortar was made from lime No. 6 (a quicklime) by using an amount such that the weight of $Ca(OH)_2$ equivalent to the weight of CaO added was one-seventh of the weight of sand.

After having obtained data with the 1:3 mortars made of the cementing materials without admixtures, those cementing materials which exhibited the extreme conditions from the standpoint of volume changes subsequent to hardening of the specimens were selected for the study of admixtures and leaner mixes (1:4 mortars). Therefore in such mortars, Portland cement No. 1, masonry cement No. 10, and limes Nos. 2 and 6 were used. The proportions by volume in the mortar admixtures were: 1 lime:1 cement:6 sand, 1 lime:1 cement:8 sand, and 2 lime:1 cement:9 sand.

The weight of calcium stearate when added to the cementing materials (in the laboratory) was 2 per cent of the combined weight of cementing materials alone. Masonry cement No. 9 contained calcium stearate, which was incorporated at the factory, and its exact quantity is not known.

(2) MIXING WATER.—The amount of mixing water required to produce "standard consistency" was determined in each case prior to making the mortar specimens. The procedure followed was the "flow-table method" described in sections F3g(3)a and F3g(3)b, Federal Specification (revised) SS–C–181 for cement, masonry. The "flow" is determined by measuring the increase in diameter of a mass of mortar after removing a mold containing it on the flat, circular top of a table and dropping the table through a height of one-half inch 25 times in 25 seconds.

(3) METHODS OF MOLDING TEST SPECIMENS—(a) *Specimens for the study of initial shrinkage.*—Six specimens 1 by 1 inch by 10 inches were made for each mortar in the study of changes in length during the period of hardening. The brass molds in which these specimens were formed were about a half-inch longer than the specimens. This half-inch difference allowed space for two glass plates, each one-fourth inch in thickness, to be cemented on the ends of the specimens. The centers of the plates were marked, and measurements were taken between the mark on one plate and that on the other

All hydrated limes were soaked in the mixing water in air-tight containers for a period of 48 hours before specimens were molded. The quicklime (lime No. 6) was soaked in this manner for two weeks.

After lubricating their inner metal surfaces the molds were put on glass plates, which were covered with waxed paper. The molds were then filled with the mortar. Tamping and troweling were avoided.

(b) *Specimens for the study of volume changes subsequent to hardening.*—Six specimens for each mortar were made in steel frames (5 by 23 inches by 1 inch) resting on glass plates covered with waxed paper. In this case there were two ¾ by ¾ by ¼ inch glass plates cemented into each end of the specimens near the corners. These afforded smooth contact points for extensometer readings and two different readings between two different pairs of contact points could be taken. After filling the frames with mortar, two ¼-inch glass rods covered with waxed paper were stuck perpendicularly through the 1-inch thick slab of fresh mortar. The rods when so placed were 20 inches apart and each was centered at 1½ inches from the end of the specimen. The two metal points of a 20-inch strain gage served to mark the positions for the glass rods.

When the mortar specimens had hardened sufficiently the glass rods were removed and brass screws were put in the holes. The head of each screw contained a countersunk hole. The points of the strain gage could be made to fit into the holes in the two screws, 20 inches apart. The screws were fixed firmly in place with a paste of litharge-glycerin cement.

(4) NUMBER OF TEST SPECIMENS.—The total number of specimens was 540, the number of mortars, 45. The nature of the mortars is indicated in Table 2.

TABLE 2.—*Mortars*

| Cementing materials | Proportions by volume | Number of test specimens | Mortar No. |
|---|---|---|---|
| Limes 1 to 7, inclusive | 1L:3S | 84 | 1 to 7, inclusive. |
| Portland cements 1 to 11, inclusive | 1PC:3S | 144 | 8 to 18, inclusive. |
| Masonry cements 1 to 10, inclusive | 1MC:3S | 108 | 19 to 28, inclusive. |
| Lime No. 2 | 1L:4S | 12 | 29. |
| Lime No. 6 | 1L:4S | 12 | 30. |
| Portland cement No. 1 | 1PC:4S | 12 | 31. |
| Masonry cement No. 10 | 1MC:4S | 12 | 32. |
| Masonry cement No. 1 | 1MC:4S | 12 | 33. |
| Masonry cement No. 2 | 1MC:4S | 12 | 34. |
| Lime No. 6 and Portland Cement No. 1 | 1L:1PC:6S | 12 | 35. |
| Lime No. 6 and Portland cement No. 1 | 2L:1PC:9S | 12 | 37. |
| Lime No. 2 and masonry cement No. 10 | 1L:1MC:6S | 12 | 38. |
| Lime No. 2 and masonry cement No. 10 | 1L:1MC:8S | 12 | 39. |
| Lime No. 2 and masonry cement No. 10 | 2L:1MC:9s | 12 | 40. |
| Portland cement No. 1 | 1PC:3S and calcium stearate.[1] | 12 | 41. |
| Portland cement No. 1 | 1PC:4S and calcium stearate.[1] | 12 | 42. |
| Masonry cement No. 10 | 1MC:3S and calcium stearate.[1] | 12 | 43. |
| Lime No. 6 and Portland cement No. 1 | 1L:1PC:6S and calcium stearate.[1] | 12 | 44. |
| Lime No. 6 and Portland cement No. 1 | 1L:1PC:8S and calcium stearate.[1] | 12 | 45. |

[1] The amount of dry calcium stearate added was 2 per cent of the weight of cement or of the combined weights of lime and cement when both were used.

### (b) BRICK SPECIMENS

Twenty-four bricks were selected from each of the eight makes of brick described in Table 1. Twelve of these were taken from the hardest and 12 from the softest burned brick of the shipment. These selections were based on visual inspection and not on absorption measurements. It was proposed to observe any expansion on wetting or contraction on drying which these bricks might undergo and, hence it was necessary to start with material which had not been exposed to moisture. Absorption was, however, determined with other soft and hard burned bricks (of each shipment) similar to the ones used in the study of volume changes. The total absorptions, expressed in per cent of initial dry weights for each make of brick have been given in Table 1. In obtaining these values, the bricks were dried at about 150° C. to constant weight and were then immersed in water at room temperature for 48 hours.

Three bricks were used to form a specimen. After drying at 150° C. to constant weight (very little moisture was found to be present), the ends of the brick were roughened and joined together with a paste of litharge-glycerin cement. This was done with the bricks lying flat side down on level boards. While the cement was plastic, bench clamps served to squeeze the ends of the bricks tightly together and reduce the thickness of the joint. The combined thickness of the two joints in a specimen was about one-eighth inch. Any shrinkage or expansion in the cementing material could, therefore, introduce only a very small error. Holes 20 inches apart were then drilled in the end bricks. Screws with heads drilled and countersunk were cemented into these holes with the litharge cement.

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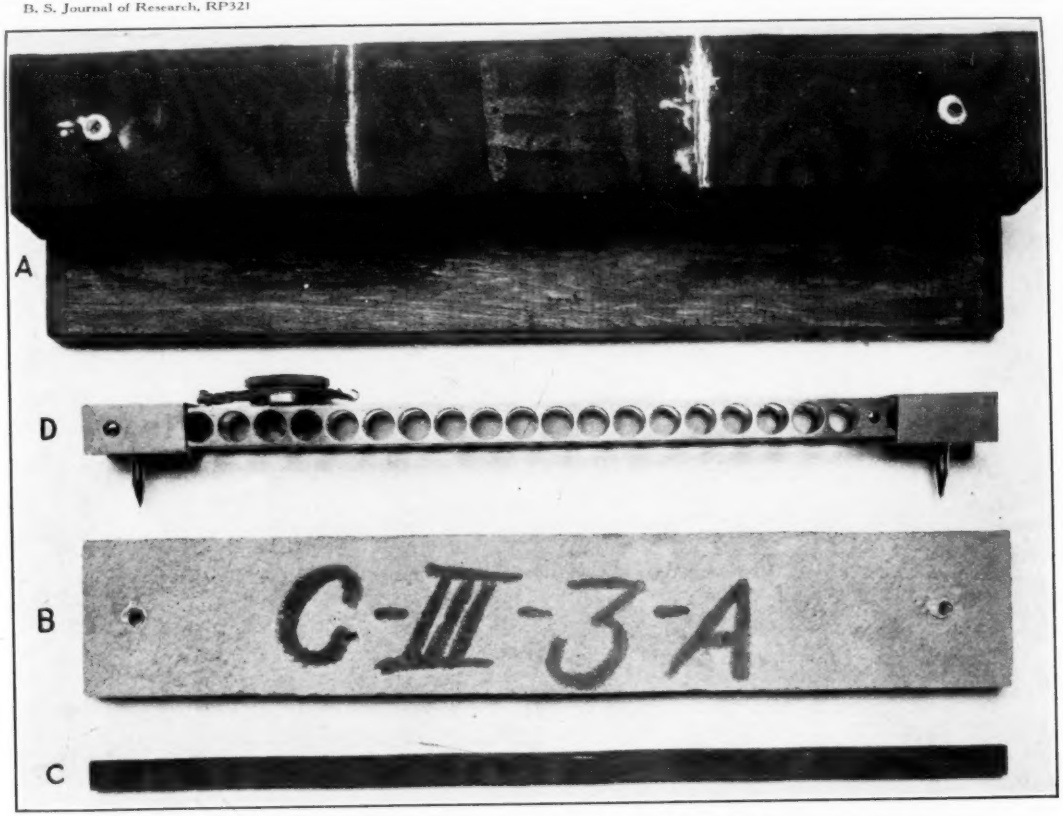


FIGURE 1.—*Materials and instruments used in the study of linear changes*

*a*, Brick specimen; *b*, mortar specimen; *c*, invar steel bar; *d*, strain gage.

In Figure 1, *a* is a brick specimen, *b* is a 1 by 5 by 23 inch mortar specimen, *c* is the standard invar steel bar for reference, and *d* is the 20-inch Whittemore type strain gage. Four specimens were made with the soft and four with the hard burned bricks with each of the eight types of brick. Two specimens were used in the study of volume changes produced by wetting and drying and two were reserved for the study both of thermal change (on the dry specimens) and freezing and thawing of moisture-saturated specimens.

## 2. EXPOSURE OF TEST SPECIMENS

### (a) MORTARS

(1) TEST SPECIMENS FOR THE STUDY OF SHRINKAGE DURING HARDENING.—The specimens were removed as soon as made to a room wherein the relative humidity was $60 \pm 5$ per cent and the temperature was $21 \pm 2°$ C. They remained here for a period of 10 days. The lengths of the specimens were measured at the end of 48 hours and 10 days.

(2) TEST SPECIMENS FOR THE STUDY OF LINEAR CHANGES SUBSEQUENT TO HARDENING.—(a) *Mortars containing either masonry or Portland cement.*—Test specimens containing cement (that is, either straight Portland or masonry cement mortars or admixtures of lime and cement) were stored under water (frequently changed) when 48 hours old. They remained so immersed for 3 months, when they were removed and placed on edge in front of an electric fan to remove the bulk of the water. When this was accomplished the specimens were placed flat side down on dry sand in metal trays. The trays and specimens were placed in a drying oven, the temperature of which was maintained at 38° C. and seldom varied more than ½° C. A metal tray containing granulated calcium chloride was placed in the bottom of the oven. An electric fan within the oven operated continuously and served to keep the relative humidity uniform throughout. It seldom exceeded 25 per cent. Usually it ranged from 20 to 25 per cent.

The specimens were removed from the oven when it was noted that during the course of a week there was no change in length of a specimen greater than 0.0004 of an inch. The specimens were then returned to the laboratory and put in water where they were kept for another three months. They were then removed and again dried to "constant length" in the oven and returned again to water.

(b) *Mortars containing only lime and sand.*—The specimens (1 inch by 5 by 23 inches) containing lime and sand alone were quite fragile during the first week or 10 days after they were formed. For this reason no attempt was made to handle them during the first 10 days, after which the brass screws for gage readings were fastened in the specimens. They then remained on glass plates for three months, exposed to the air of the laboratory. The average relative humidity of the laboratory during a year was between 35 and 50 per cent, and varied from 18 to 80 per cent. The temperature varied from 15° to 32° C., the average being about 19° C.

After three months' storage in the laboratory, the lime-mortar specimens were taken to a room wherein the relative humidity was approximately 95 per cent and the temperature was $21° \pm 1°$ C., and for three months were daily sprinkled. At the end of this period, they were dried first in the air of the laboratory, using a fan to cir-

culate the air rapidly about them. When the bulk of moisture had been removed in this way, the specimens were dried at 38° C. in the constant-temperature oven for a period of time such that during a week the change in length was not greater than 0.0004 inch.

After drying, the specimens were placed in metal trays and kept about half submerged in water. Complete immersion was impracticable, for in this case the specimens became soft. Care was taken to keep the water level fairly constant. Water rose by capillarity and kept the lime-mortar specimens saturated. At the same time, the hardening process could take place to some extent at least. After soaking in this manner for three months the specimens were again dried to "constant length."

(3) Changes in Length Due to Thermal Change.—After one of the oven dryings, three of the six specimens were left for one day in the laboratory, gage readings were taken, and the specimens were then placed in a freezing room, the temperature of which ranged from −12° to −5° C. They remained here for at least 12 hours and linear measurements were again made. If the data for each of the specimens were not in fairly good agreement, the entire procedure was repeated until results checked reasonably well. The temperature difference between the laboratory and freezing room varied from 28° to 36° C.

#### (b) BRICK SPECIMENS

(1) Wetting and Drying.—The lengths of the brick specimens were first determined when dry and again after a month in water at room temperature. The specimens were then dried for a week at 150° C., removed, cooled to room temperature, and again measured. This procedure was then repeated once.

(2) Freezing and Thawing.—The dry brick specimens were immersed for 48 hours in water at room temperature, removed to the freezing chamber for 18 hours, and then thawed under water at room temperature for six hours. The freezing and thawing was continued until the specimens showed disintegration or had endured 20 cycles. After freezing and thawing, the specimens were dried at 150° C. for a period of one week. Gage readings were taken before putting the dry specimens in water, after 48 hours' soaking, after each freezing, after each thawing, and after the oven-dried specimens had cooled.

(3) Thermal Change.—The specimens were kept dry throughout these tests. They were removed from the laboratory to the freezing room, where they remained for at least 12 hours. They were then returned to the laboratory and the cycle was repeated several times. The laboratory and freezing room temperatures were recorded at the time strain gage readings were taken.

### 3. MEASUREMENTS

#### (a) MORTAR SPECIMENS

(1) The Study of Initial Shrinkage.—Measurements with micrometer calipers reading to 0.001 inch were made at the end of 48 hours and again at the end of 10 days' storage in the constant temperature-constant humidity room.

(2) The Study of Linear Changes Subsequent to Hardening.—During the three months storage in water, linear changes were

measured from time to time. No reading was taken on the specimens until the water in which they were immersed had been at about 25° C. for at least one hour. By carefully mixing hot and cold water, the temperature could be maintained at very approximately 25° C.

Extensometer readings in addition to strain-gage readings were taken on the last day of each successive exposure (wetting and drying). Strain-gage readings were taken frequently during these procedures. The strain gage and extensometer were each equipped with dials reading to 0.0001 inch. The former was checked from time to time with an Anderson screw, a device for dial calibration.

A strain-gage reading could be taken within a few seconds time and specimens removed from the drying oven (temperature 38° C.) did not cool appreciably while being measured. The readings at 38° C. were computed to values that would have been obtained had the specimens been cooled to 25° C. These computations were based on data obtained from the study of the effect of thermal change on the linear expansion and contraction of the specimens. These temperature corrections for the different mortars were relatively small in all cases.

A temperature correction was also made when lime mortar specimens were measured during their initial three months' storage in the laboratory. This was done whenever laboratory temperature differed from 25° C. by an amount greater than 3° C.

#### (b) BRICK SPECIMENS

The procedure followed in measuring the linear changes in the brick specimens was, in so far as the tests were similar, the same as that described for mortars.

## III. RESULTS

### 1. MORTARS

#### (a) INITIAL SHRINKAGE

(1) 1:3 MORTARS.—The shrinkages of the various 1:3 mortars are given in Table 3. These data include values obtained at the end of 48 hours and 10 days for all 1:3 mortars. Shrinkage is expressed in terms of per cent change in length.

The data of Table 3 indicate a relatively wide variation in the initial shrinkages among the different masonry cements. There was not such a wide variation when the various lime and Portland cement mortars are considered.

It may be noted that the amount of shrinkage of the lime specimens at the end of 48 hours was from 75 (lime No. 4) to 86 per cent (lime No. 6) of the total shrinkage during the 10-day period. After 10 days, the lime-mortar specimens were apparently not as hard as were the Portland cement mortars when 48 hours old. The linear shrinkages of the cement mortars were more nearly completed at the end of 48 hours.

TABLE 3.—*Shrinkage of 1:3 mortars during early hardening*

(Averages for six specimens. The maximum deviation from any average value, considering all mortars, was approximately 15 per cent)

| Class of mortars | Cementing material | Decrease in initial length— | |
|---|---|---|---|
| | | During 48 hours | During 10 days |
| | | *Per cent* | *Per cent* |
| 1 lime:3 sand | Lime No. 1 | 0.41 | 0.49 |
| | Lime No. 2 | .49 | .60 |
| | Lime No. 3 | .30 | .37 |
| | Lime No. 4 | .38 | .51 |
| | Lime No. 5 | .49 | .59 |
| | Lime No. 6 | .55 | .64 |
| | Lime No. 7 | .45 | .58 |
| 1 P. C.:3 sand | P. C. No. 1 | .22 | .23 |
| | P. C. No. 2 | .15 | .17 |
| | P. C. No. 3 | .12 | .14 |
| | P. C. No. 4 | .17 | .19 |
| | P. C. No. 5 | .13 | .16 |
| | P. C. No. 6 | .13 | .15 |
| | P. C. No. 7 | .14 | .15 |
| | P. C. No. 8 | .14 | .15 |
| | P. C. No. 9 | .27 | .30 |
| | P. C. No. 10 | .11 | .11 |
| | P. C. No. 11 | .19 | .21 |
| 1 M. C.:3 sand | M. C. No. 1 | .24 | .29 |
| | M. C. No. 2 | .20 | .22 |
| | M. C. No. 3 | .31 | .33 |
| | M. C. No. 4 | .61 | .68 |
| | M. C. No. 5 | .19 | .21 |
| | M. C. No. 6 | .33 | .37 |
| | M. C. No. 7 | .39 | .43 |
| | M. C. No. 8 | .40 | .44 |
| | M. C. No. 9 | .99 | 1.11 |
| | M. C. No. 10 | .26 | .30 |

The variations of shrinkage during early hardening produced by changing the relative proportions by volume of cementing materials and sand are illustrated in Figure 2. The various points in this diagram represent average values as obtained with the six specimens of each mortar. The numbers at these points designate the mortars as listed in Table 2. Figure 2 also shows the effect of calcium stearate on the early shrinkage of a few representative mortars.

The lengths of the vertical lines above and below each point represent the maximum positive and negative deviations from the average shrinkage of the six individual specimens of each mortar.

(2) 1:4 MORTARS.—The "best" and the "poorest" cements (Portland cement No. 1 and masonry cement No. 10, respectively) and limes (Nos. 6 and 2, respectively) were selected on the basis of volume changes occurring subsequent to hardening. The initial shrinkages of the 1:3 as compared with the 1:4 mortars made with these materials may be noted in Figure 2.

The initial shrinkage in the 1:4 was less than that in the 1:3 mortars in all cases. This difference was greater in the masonry and Portland cement than it was in the lime mortars.

(3) LIME AND CEMENT MORTARS.—Mortar Nos. 37 and 40 were richer in lime than Nos. 35 and 38, respectively (fig. 2), and it is seen that the shrinkage during early hardening increases with the lime content. Mortars 36 and 39 were 1:1:8 mortars, lean both in lime

and cement. Their initial shrinkages were lower than those of the 1:1:6 mortars (Nos. 35 and 38).

(4) WATER REPELLENT MATERIALS.—The effect on initial shrinkage produced by adding water repellent substances was not given much attention in this investigation. The subject has been studied by others[9] and the results indicate that the effect in so far as the magnitude of the volume changes is concerned is very small.

Mortar No. 18 (fig. 2) was made from Portland cement No. 11 containing no water-repellent substance. Mortar No. 20 was made from masonry cement No. 2 and contained calcium stearate added

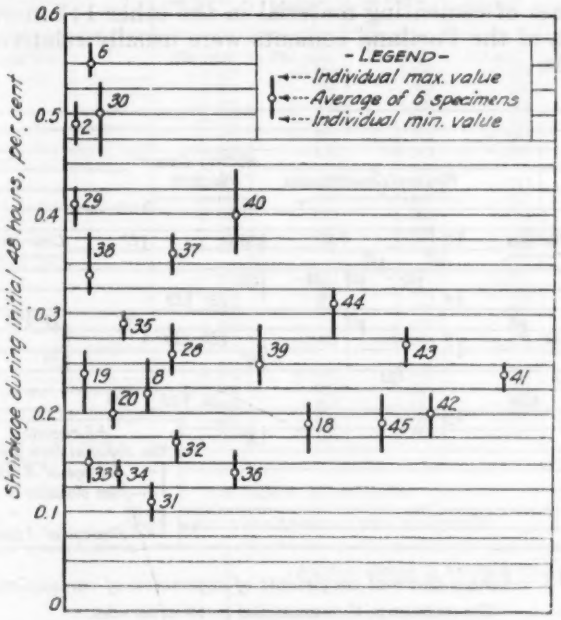


FIGURE 2.—*Linear shrinkage of mortars during early hardening*

at the same factory (amount not determined) where Portland cement No. 11 was produced. The initial shrinkages of these two mortars were very nearly the same. Mortar Nos. 41, 42, 43, 44, and 45 (fig. 2) containing calcium stearate may be compared with mortar Nos. 8, 31, 28, 35, and 36, respectively. The former contained calcium stearate, whereas the latter did not. In this case, the stearate was added to the cementing materials in the laboratory. The differences are not appreciable.

### (b) EFFECT OF THERMAL CHANGE

The linear changes produced by subjecting dry mortar specimens to changes in temperature may be seen in Figure 3. As in Figure 2, the points in Figure 3 represent averages (in this case the average is for three specimens) and the maximum deviation in each case is represented by the length of the vertical line which extends upward

[9] See footnote 7, p. 1004.

or downward from the point to show the direction of departure. The numbers in Figure 3 designate the mortars listed in Table 2.

$C$, the linear thermal coefficient, is equal to $\frac{\Delta L}{L\Delta t}$ where $\Delta L$ is the change in length of $L$ during a change in temperature of $\Delta t°C$. In Figure 3, the values of $C$ are multiplied by $(10)^5$ The thermal coefficients of the 1 : 3 Portland cement mortars were as a whole slightly higher than those of the 1 : 3 lime or masonry cement mortars. This may have been due to the fact that the actual mass of cementing material in the 1 : 3 Portland cement mortars was relatively greater than the mass of cementing material in the other 1 : 3 mortars, since the densities of the Portland cements were usually relatively greater in most cases.

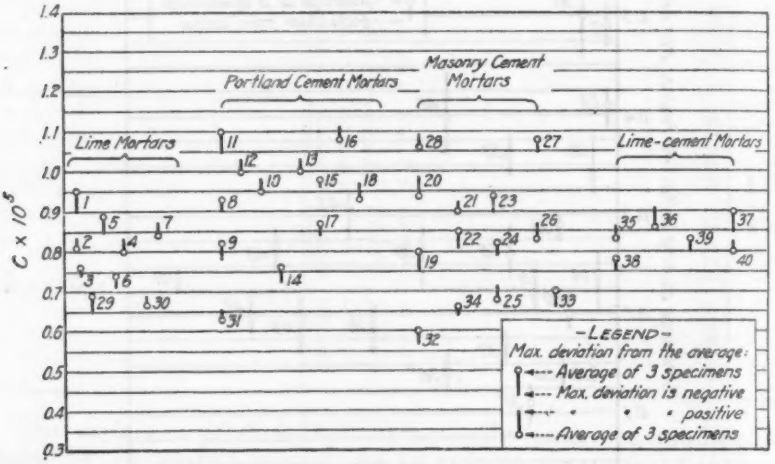


FIGURE 3.—*Linear thermal coefficients of expansion of various mortars*

The coefficients, C, is multiplied by $10^5$ in the sales.

In Figure 3, Nos. 29, 30, 31, 32, 33, and 34 represent the thermal coefficients of the 1 : 4 mortars, and it may be noted these are among the lowest values obtained.

### (c) ALTERNATE WETTING AND DRYING

(1) 1:3 MORTARS.—The linear changes of the 1:3 mortar specimens, produced by varying the moisture content, appear in Table 4. All values in the second column are with reference to the last readings taken immediately prior to beginning the first exposure. All values in the third column are with reference to the last readings taken on the last day of the first exposure, etc. For example, after the six specimens of Portland cement No. 6 had been in water for three months they were (on the average) 0.009 per cent longer than they were a few minutes before they were first immersed in water. After the first drying (third column) they were 0.095 per cent shorter than they were when removed from water for the first time, etc.

TABLE 4.—*Linear changes in 1 : 3 hardened mortar specimens subjected to alternate wetting and drying*

[+ denotes expansion, − denotes shrinkage. Values are averages of results obtained with 6 specimens. The maximum deviation from any average value, considering all mortars, was approximately 10 per cent.]

1:3 PORTLAND AND MASONRY CEMENT MORTARS

(Tests begun when specimens were 48 hours old)

| Cementing material | Average change in length of specimens during each exposure— | | | | | |
|---|---|---|---|---|---|---|
| | 3 months in water | Dried to "constant length" | 3 months in water | Dried to "constant length" | Third soaking period | |
| Portland cement No.: | *Per cent* | *Per cent* | *Per cent* | *Per cent* | *Months* | *Per cent* |
| 1 | +0.005 | −0.079 | +0.059 | −0.057 | 5 | +0.066 |
| 2 | +.014 | −.088 | +.063 | −.062 | 5 | +.068 |
| 3 | +.028 | −.080 | +.059 | −.056 | 5 | +.058 |
| 4 | +.006 | −.087 | +.064 | −.064 | 5 | +.065 |
| 5 | +.016 | −.094 | +.063 | −.054 | 5 | +.059 |
| 6 | +.009 | −.095 | +.062 | −.051 | 5 | +.055 |
| 7 | +.012 | −.082 | +.054 | −.047 | 3 | +.052 |
| 8 | +.017 | −.090 | +.057 | −.055 | 3 | +.059 |
| 9 | +.028 | −.084 | +.061 | −.058 | 3 | +.055 |
| 10 | +.023 | −.095 | +.064 | −.060 | 3 | +.058 |
| 11 | +.028 | −.101 | +.070 | −.066 | 3 | +.073 |
| Masonry cement No.: | | | | | | |
| 1 | +.020 | −.055 | +.046 | −.051 | 6 | +.051 |
| 2 | +.025 | −.108 | +.064 | −.060 | 6 | +.073 |
| 3 | +.043 | −.085 | +.070 | −.050 | 4 | +.059 |
| 4 | +.030 | −.085 | +.058 | −.046 | 4 | +.049 |
| 5 | +.015 | −.082 | +.065 | −.054 | 4 | +.058 |
| 6 | +.040 | −.076 | +.054 | −.048 | 4 | +.043 |
| 7 | +.003 | −.065 | +.038 | −.041 | 4 | +.046 |
| 8 | +.006 | −.074 | +.045 | −.042 | 4 | +.042 |
| 9 | +.031 | −.054 | +.041 | −.034 | 4 | +.036 |
| 10 | +.029 | −.164 | +.082 | −.077 | 3 | +.074 |

1:3 LIME MORTARS

(Tests begun when specimens were 10 days old)

| Cementing material | Average change in length of specimens during each exposure— | | | | |
|---|---|---|---|---|---|
| | 3 months in air (laboratory) | 3 months in humid room, sprayed daily | Dried to "constant length" | 3 months partially immersed in water | Dried to "constant length" |
| Lime No.: | *Per cent* | *Per cent* | *Per cent* | *Per cent* | *Per cent* |
| 1 | +0.008 | +0.027 | +0.004 | +0.003 | No change. |
| 2 | +.002 | +.071 | −.004 | +.019 | +0.004 |
| 3 | +.008 | +.021 | −.017 | +.011 | +.006 |
| 4 | +.003 | +.036 | −.002 | +.003 | −.002 |
| 5 | +.004 | +.014 | −.004 | +.002 | −.004 |
| 6 | No change. | +.008 | [1] −.001 | +.002 | −.004 |
| 7 | −.004 | +.022 | −.007 | [1] +.001 | +.003 |

[1] About the magnitude of the probable error in measurement.

It is noted that the volume changes in the 1:3 lime mortars were generally appreciably less than those characteristic of masonry and Portland cement mortars under very similar conditions.

The alternate shrinkages on drying and expansion on wetting the cement mortars are comparable to data obtained by others. It is interesting to note that the general tendency of the lime mortars was to expand even under drying conditions in some instances. Thus,

there was no shrinkage whatever in lime No. 1 mortar. During the entire period of test (approximately one year) lime No. 1 specimens expanded 0.042 per cent. The net volume change obtained with mortar specimens made from lime No. 6 was an expansion of 0.005 per cent. This was less than one-tenth of the expansion of the various Portland cement mortars during three months' immersion in water.

The expansion of the Portland and masonry cement mortars during the first 24 hours' soaking following a drying period varied from 0.02 to 0.05 per cent. The rate of expansion of the lime mortars was very much less than this. The comparative rates and magnitudes of changes in length of 1:3 mortar specimens made from limes Nos. 2 and 6, Portland cement No. 1 and masonry cement No. 10 may be noted in Figure 4. The full lines in each curve denote linear changes

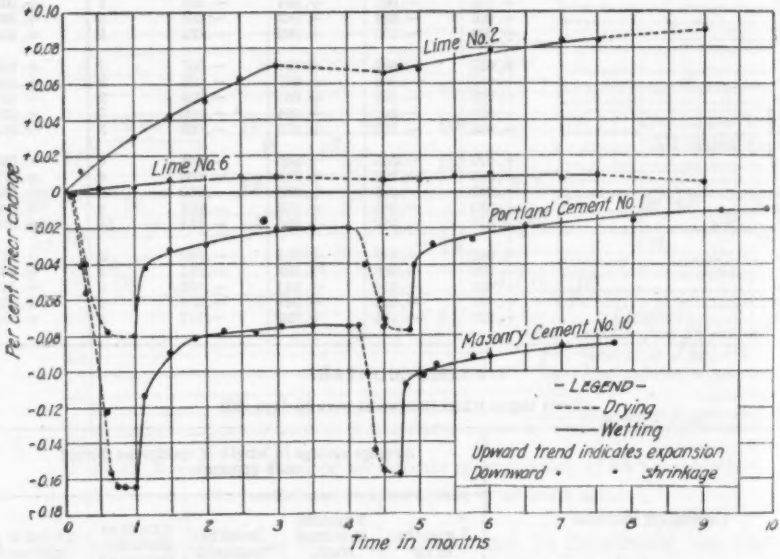


FIGURE 4.—*Linear changes in hardened mortar specimens*

Tests begun when specimens were three months old.

during wetting and the broken lines denote such changes during the drying periods. The origin is the average of the readings of the six specimens of each mortar taken at the beginning of the second exposure (column 3, Table 4); that is, the specimens at this point (the origin) were three months old. The 1:3 lime mortars were kept saturated during the second exposure, whereas the 1:3 Portland cement mortars were dried to "constant length." The drying procedure was not continued over any definite period of time. Drying was discontinued where during a period of one week the linear change in a specimen did not exceed 0.0004 inch per 20 inches.

(2) 1:4 MORTARS.—Linear changes produced by alternately wetting and drying the 1:4 mortars are presented in Table 5. A comparison of the data in this table with the data in Table 4 for the same cementing materials indicates that with the possible exception of lime No. 6,

the magnitude of shrinkage on drying and expansion on wetting was less in the 1:4 than in the 1:3 mortars. The difference, although appreciable, hardly warrants a preference of the 1:4 mortars from this standpoint alone. The mason usually experiences more difficulty in troweling the leaner mixes, and this fact must also be considered. The linear expansion and shrinkage both in 1:3 and 1:4 mortars made with lime No. 6 were relatively small. The fact that the linear changes were slightly higher in the latter case may not, therefore be significant.

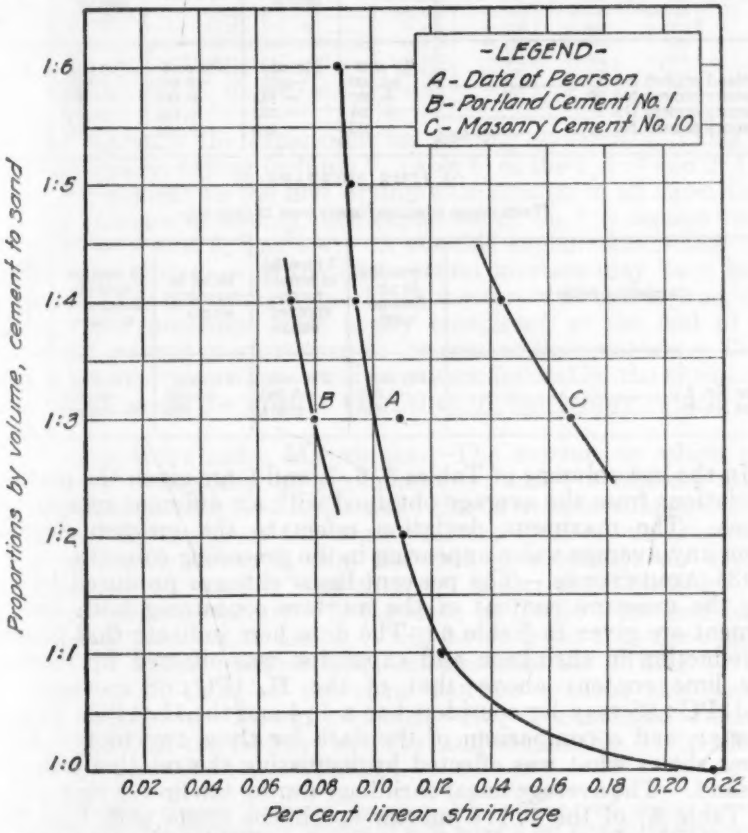


FIGURE 5.—*Variations in linear shrinkage produced by changing the relative proportions by volume of cement and sand*

Curve *A* of Figure 5 is obtained by plotting the data of Pearson.[10] The small portions of curves B and C are obtained by plotting the data relative to Portland cement No. 1 and masonry cement No. 10 (third column, Tables 4 and 5). The curve obtained by plotting Pearson's data indicates a sharp decrease in the effect of leanness on linear shrinkage above the point designating 1:1 mortar.

[10] See footnote 2, p. 1004.

TABLE 5.—*Linear changes produced by alternately wetting and drying 1:4 mortars subsequent to hardening*

[Averages of 6 specimens; + denotes expansion, − denotes shrinkage]

1:4 PORTLAND AND MASONRY CEMENT MORTARS

(Tests begun when specimens were 48 hours old)

| Cementing material | 3 months in water | Dried to "constant length" | 3 months in water | Dried to "constant length" | Maximum deviation from any average value |
|---|---|---|---|---|---|
| | *Per cent* | *Per cent* | *Per cent* | *Per cent* | *Per cent* |
| Portland cement No. 1 | +0.009 | −0.071 | +0.042 | −0.040 | 6 |
| Masonry cement No. 10 | +.007 | −.145 | +.080 | −.078 | 14 |
| Masonry cement No. 1 | +.024 | −.035 | +.026 | −.021 | 10 |
| Masonry cement No. 2 | +.012 | −.090 | +.051 | −.047 | 12 |

1:4 LIME MORTARS

(Tests begun when specimens were 10 days old)

| Cementing material | 3 months in air (laboratory) | 3 months in humid room, sprayed daily | Dried to "constant length" | 3 months partially immersed in water | Maximum deviation from any average value |
|---|---|---|---|---|---|
| | *Per cent* | *Per cent* | *Per cent* | *Per cent* | *Per cent* |
| Lime No. 2 | −0.002 | +0.040 | −0.005 | +0.019 | 20 |
| Lime No. 6 | −.010 | +.011 | −.002 | No change. | 8 |

In the last columns of Tables 5, 6, 7, and 8 are given the maximum deviations from the average obtained with six different mortar specimens. The maximum deviation refers to the greatest departure from any average value appearing in the preceding columns.

(3) ADMIXTURES.—The per cent linear changes produced by varying the moisture content of the mortars containing both lime and cement are given in Table 6. The data here indicate that generally a reduction in shrinkage and expansion was effected by increasing the lime content above that of the 1L:1PC:6S mortars. The 1L:1PC:8S may be considered as a 1:4 and the 1L:1PC:6S as 1:3 mortar, and a comparison of the data for these two mortar admixtures shows what was effected by increasing the relative proportion of sand. The average linear shrinkage during the first drying (column 5, Table 6) of the 1:1:6 mortar specimens made with lime No. 6 and Portland cement No. 1 was greater (Table 4, column 3) than that of the 1:3 Portland cement No. 1 mortar specimens. From the data of Tables 4 and 6 it is seen that the reverse was true in the case of lime No. 2 and masonry cement No. 10.

TABLE 6.—*Linear changes produced by alternately wetting and drying mortars containing both lime and cement*

[Tests begun when specimens were 48 hours old (average values for 6 specimens; + denotes expansion; − denotes shrinkage)]

| Lime | Cement | Proportions by volume | 3 months in water | Dried to "constant length" | 3 months in water | Dried to "constant length" | Maximum deviation from any average value |
|---|---|---|---|---|---|---|---|
| | | | *Per cent* | *Per cent* | *Per cent* | *Per cent* | *Per cent* |
| No. 6 | PC No. 1 | 1L:1PC : 6S | +0.007 | −0.111 | +0.050 | −0.043 | 8 |
| | | 2L:1PC : 9S | +.018 | −.069 | +.042 | −.032 | 10 |
| No. 2 | MC No. 10 | 1L:1MC : 6S | +.015 | −.126 | +.049 | −.046 | 6 |
| | | 2L:1MC : 9S | +.013 | −.072 | +.034 | −.031 | 15 |
| No. 6 | PC No. 1 | 1L:1PC : 8S | +.008 | −.068 | +.042 | −.041 | 7 |
| No. 2 | MC No. 10 | 1L:1MC : 8S | +.007 | −.085 | +.045 | −.037 | 12 |

On the contrary the expansions on wetting (column 6, Table 6) and shrinkages on drying (column 7, Table 6) of the 1:1:6 and 2:1:9 mortars subsequent to the first drying were smaller in all cases than the linear changes attending such exposures of the 1:3 cement mortars (columns 4 and 5, Table 4). A possible explanation is that the rate of initial shrinkage of the lime-cement mortars may have been less than that of the cement (no lime) mortars. If this is true, the shrinkage was probably more nearly completed at the end of 48 hours in the cement mortars than in the cement-lime mortars. Then during a later period, when conditions were favorable, the shrinkage of the latter would be greater than that of the former, which was the case.

(4) WATER-REPELLENT MATERIALS.—The mortars to which calcium stearate was added in the laboratory, and 1:3 mortars made with masonry cement No. 2, did not differ in volume change during wetting and drying from the same mortars without the stearate. It was indicated, however, that the rate of shrinkage on drying and expansion on wetting was to some extent diminished by the presence of calcium stearate. If the data of Table 7 are compared with those of Tables 4, 5, and 6, it will be observed that the magnitudes of the linear changes with calcium stearate (Table 7) are comparable with those of the same mortars without this water-repellent substance. Masonry cement No. 2 contained calcium stearate, added at the factory, and Portland cement No. 11 (made at the same factory) did not. (Table 4.)

TABLE 7.—*Linear changes produced by alternately wetting and drying mortars containing calcium stearate, the amount of such being 2 per cent of the total weight of cementing materials*

[Tests begun when specimens were 48 hours old. (Average values for 6 specimens; + denotes expansion, − denotes shrinkage.)]

| Cementing material | Proportions by volume | 3 months in water | Dried to "constant length" | 3 months in water | Dried to "constant length" | Maximum deviation from any average value |
|---|---|---|---|---|---|---|
| | | *Per cent* | *Per cent* | *Per cent* | *Per cent* | *Per cent* |
| Portland cement No. 1 | 1PC:3S | +0.012 | −0.081 | +0.054 | −0.053 | 9 |
| Masonry cement No. 10 | 1MC:3S | +.024 | −.166 | +.084 | −.072 | 7 |
| Portland cement No. 1 | 1PC:4S | +.007 | −.074 | +.041 | −.045 | 6 |
| Lime No. 6; Portland cement No. 1 | 1L:1PC:6S | +.010 | −.116 | +.053 | −.040 | 12 |
| Do | 1L:1PC:8S | +.006 | −.065 | +.040 | −.048 | 5 |

In Table 8 are given the average percentage linear expansions of certain mortars, with and without calcium stearate, during the first 24 hours in water following the first oven drying.

TABLE 8.—*Linear expansion during the first 24 hours in water following the first oven drying and when specimens were approximately 4 months old*

[Average values for 6 specimens]

| Cementing materials | Proportions by volume | Linear expansion | | Maximum deviation from any average value |
|---|---|---|---|---|
| | | With calcium stearate | Without calcium stearate | |
| | | *Per cent* | *Per cent* | *Per cent* |
| Portland cement No. 1 | 1PC:3S | 0.006 | 0.019 | 20 |
| Masonry cement No. 10 | 1MC:3S | .024 | .043 | 35 |
| Portland cement No. 1 | 1PC:4S | .009 | .014 | 36 |
| Lime No. 6; Portland cement No. 1 | 1L:1PC:6S | .018 | .022 | 40 |
| Do | 1L:1PC:8S | .006 | .013 | 24 |

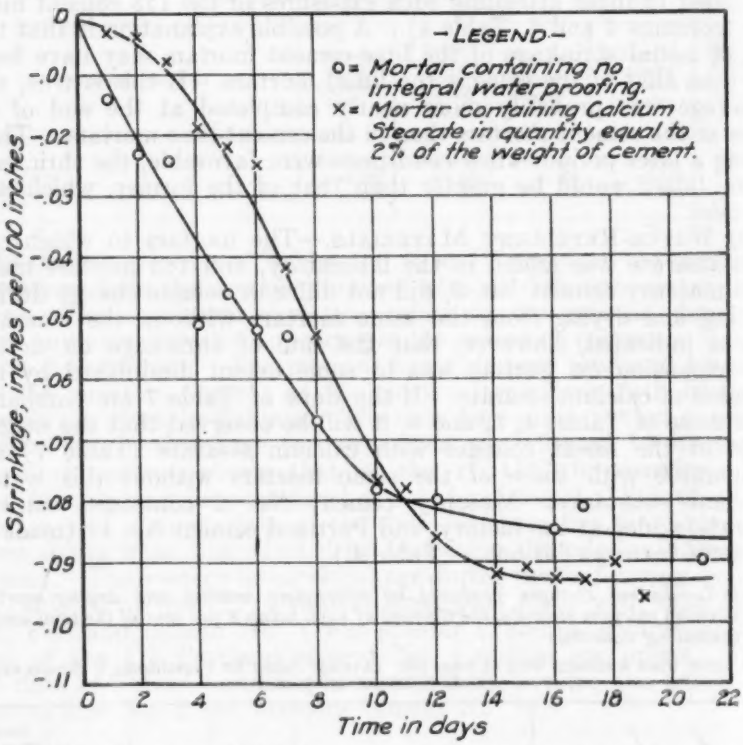


FIGURE 6.—*The effect of calcium stearate on the rate of shrinkage (on drying) of hardened mortars*

Figure 6 illustrates the shrinkage of 1:3 mortar specimens with and without calcium stearate. The curve for the mortar containing calcium stearate was obtained by plotting the average linear shrinkages from day to day of the six 1:3 specimens made with masonry cement No. 2. The other curve is descriptive of the average rate of shrinkage of the six 1:3 specimens made with Portland cement No. 11.

The data plotted in Figure 6 were obtained from strain-gage readings taken when the specimens of both mortars were being dried simultaneously at 38° C. in the oven, subsequent to drying for four days in the laboratory. The "zero" mark in the ordinate scale is the reading taken on the day the specimens were put in the oven. During the four days' drying in the laboratory there was a very small amount of shrinkage in all of the specimens. The rate of shrinkage was most rapid when the bulk of the water was removed. According to curves presented by Allan[11] the rate of shrinkage in concrete units does not become very noticeable until from 70 to 80 per cent of the moisture is lost.

It is indicated from the plotted data of Figure 6 and the tabulated data of Table 8 that the rate of linear change was diminished by the presence of calcium stearate. However, upon continued wetting or drying, the presence of the stearate had no noticeable effect on the final values obtained.

## 2. BRICK

### (a) EFFECT OF THERMAL CHANGE

The term "soft" has but little meaning when applied to materials, such as brick Nos. 2, 3, 4, 5, and 6 of Table 1. It is noted that the absorption ranges were limited in these cases. Also, strictly speaking, there were no individual bricks among the other numbers (1, 7, and 8) which could have been properly called hard burned. Among each make of brick, some samples were harder burned than others. The terms, "hard" and "soft" burned in this connection are merely relative.

The linear thermal coefficients of the relatively hard and soft burned brick of each of the eight types are given in Table 9. The lowest coefficient in this table is $0.36 \times 10^{-5}$ and the highest is $0.85 \times 10^{-5}$ per degree centigrade. The lowest values were obtained with brick Nos. 5 and 6, both made from fire clay. The highest thermal coefficients were had by brick Nos. 7 and 8, the most porous of all of the eight types of brick. With the exception of brick Nos. 7 and 8, the linear thermal coefficients of the eight makes of brick were distinctly lower than values for the 1:3 mortars, given in Figure 3.

TABLE 9.—*Linear thermal coefficients of expansion of brick*

Coefficient, $C = \frac{\Delta L}{L \Delta t}$ where $\Delta L$ is the change in length per 20 inches during a temperature $\Delta t$° C.

[Values are averages for 2 specimens of 3 bricks each]

| Brick No. | Soft or hard burned | $\Delta L$ | $\Delta t$ | $C \times 10^5$ |
|---|---|---|---|---|
| | | *Inch* | ° *C.* | |
| 1 | Hard burned | 0.0028 | 36.5 | 0.39 |
| | Soft burned | .0034 | 36.5 | .47 |
| 2 | Hard burned | .0032 | 31.0 | .52 |
| | Soft burned | .0031 | 31.0 | .52 |
| 3 | Hard burned | .0030 | 36.7 | .41 |
| | Soft burned | .0036 | 36.7 | .49 |
| 4 | Hard burned | .0032 | 34.0 | .47 |
| | Soft burned | .0034 | 34.0 | .50 |
| 5 | Hard burned | .0025 | 33.9 | .37 |
| | Soft burned | .0026 | 33.9 | .38 |
| 6 | Hard burned | .0024 | 33 9 | .36 |
| | Soft burned | .0036 | 33.9 | .38 |
| 7 | Hard burned | .0050 | 36.5 | .68 |
| | Soft burned | .0062 | 36.5 | .85 |
| 8 | Hard burned | .0040 | 28.3 | .71 |
| | Soft burned | .0041 | 28.3 | .72 |

[11] W. D. M. Allan, Shrinkage Measurements of Concrete Masonry, Proc. Am. Concrete Inst., **26**, 6, p. 699; 1930.

The average linear thermal expansion of 1:3 mortars made with masonry cement No. 5 was 0.0068 inch per 20 inches per 36° C. Brick No. 1 (hard burned) expanded 0.0028 inch per 20 inches when the temperature increased 36° C. The differential expansion between those two materials for this temperature change is computed as 0.004 inch per 20 inches.

(b) ALTERNATE WETTING AND DRYING

The expansion of the brick specimens during one month's immersion in water is designated as *A* in Figure 7. The shaded columns denote expansions of the relatively hard burned and the unshaded columns denote expansion of the relatively soft-burned bricks of each make.

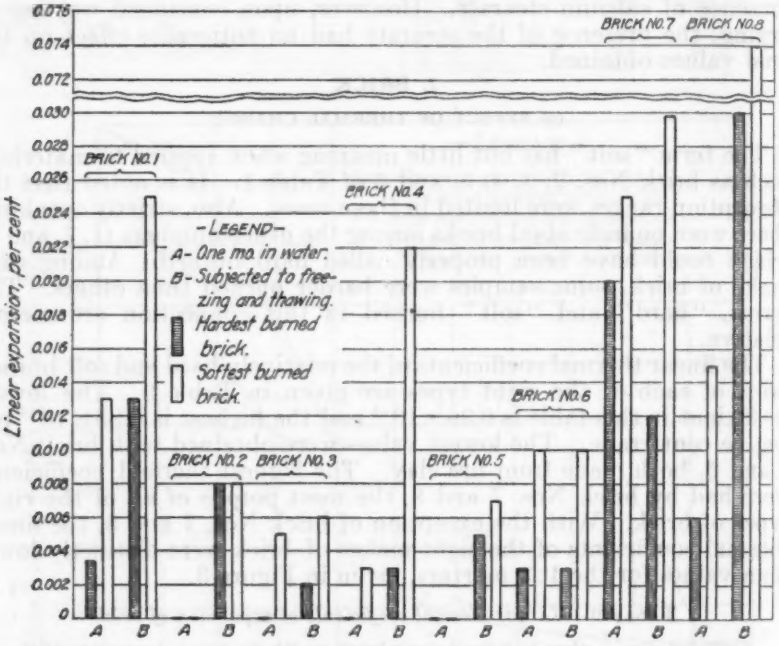


FIGURE 7.—*Linear expansions of brick specimens during wetting (A) and alternately freezing and thawing (B)*

This same designation applies to each pair of columns marked *B* (fig. 7) which represent expansions at the completion of the freezing and thawing cycles.

It is seen that neither hard nor soft-burned bricks of types 2 and 5 expanded measurably during a month's soaking. The maximum expansion produced in any case by this treatment was 0.025 per cent (soft-burned bricks of type 7). Each plotted value of Figure 7 is the average of measurements made with two specimens.

The expansions of the bricks on prolonged soaking were greatest for "salmon" or underburned bricks, and it may be that a test of this sort could serve to indicate whether or not bricks may be underburned. The specimens which expanded during a month's immersion in water did not subsequently shrink to any measureable extent when dried for one week in an oven at approximately 150°C. This same

condition existed when specimens which had expanded during freezing and thawing were subsequently dried in this manner. Holscher [12] reports similar expansions in clay bodies during autoclave treatment.

### (c) ALTERNATE FREEZING AND THAWING

The average expansion (for two specimens of three bricks each) at the completion of the freezing and thawing tests are marked *B* in Figure 7. When no disintegration occurred the specimens were subjected to from 18 to 20 cycles of freezing and thawing. Soft-burned bricks of type 7 were subjected to 10 cycles; soft-burned bricks of type 8, 2 cycles; and hard-burned bricks of type 8, 5 cycles.

It is conceivable that both brick and mortar in a masonry wall may at times become saturated with water. It is not so likely,

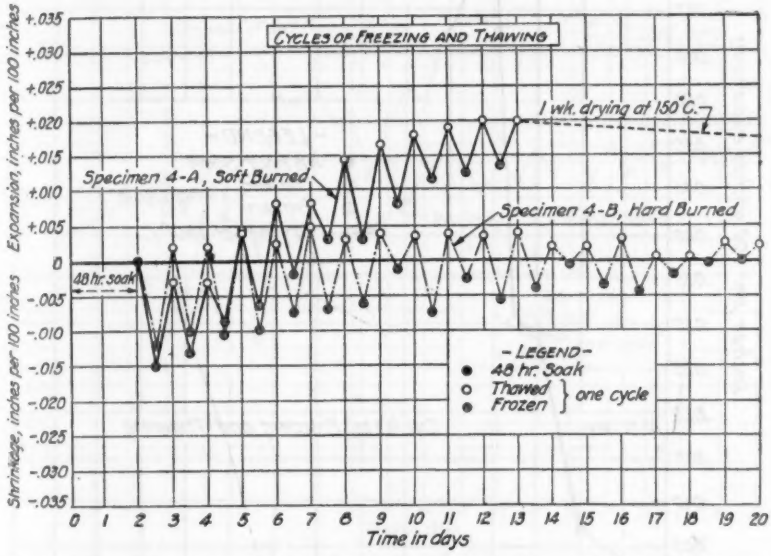


FIGURE 8.—*Linear expansion and contraction of saturated brick specimens (bricks of type 4) during alternate freezing and thawing*

The effect of moisture was greater that than of temperature changes in the case of soft-burned bricks.

however, that this moisture, saturating these materials, would be alternately frozen and thawed many times without any drying taking place. When brick are kept well saturated during freezing and thawing tests, the apparent porosity tends to increase a small amount.[13] There is a progressive increase in the extent of saturation of the brick under these conditions. After many cycles of freezing and thawing, brick contain very nearly as much water as they normally contain when kept in boiling water for five hours. It is reasonable to suppose that when there is but little pore space not filled with water the pressure produced by the water changing to ice tends to increase the size of the pore. Evidently this small distension is permanent under all normal climatic conditions.

[12] H. H. Holscher, Effects of Autoclave Treatments on Ceramic Bodies and Clays, J. Am. Ceram. Soc., **14**, 3, pp. 207–218; 1931.

[13] L. A. Palmer and J. V. Hall, Some Results of Freezing and Thawing Tests Made with Clay and Shale Brick, Proc. Am. Soc. Test. Materials, **30**, p. 767.

This slight increase in apparent porosity during progressive freezing and thawing is attended by a small and relatively slow (usually) expansion of the brick. This is illustrated in Figure 8. If the brick are not burned to the proper maturing temperature, the expansion (as well as disintegration) is rapid. The softer burned bricks of type 8 (fig. 9) began to disintegrate after the first two cycles. The graphs (figs. 8, 9, and 10), represent all of the extreme and intermediate conditions that were obtained. The specimens containing the

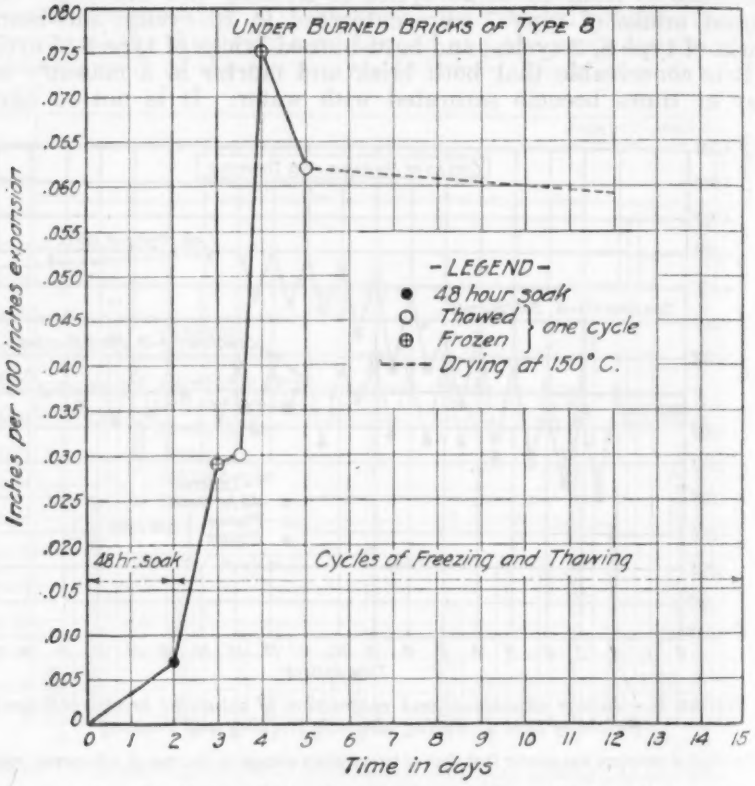


FIGURE 9.—*Rapid expansion of saturated underburned bricks during alternate freezing and thawing*

harder bricks of type 8 were very similar in their behavior during freezing and thawing to the specimens of soft-burned bricks of type 7, shown in Figure 10. The graphs of the plotted data (not given) obtained with specimens of both hard and soft-burned bricks of types 2, 3, 5, and 6 and with hard-burned bricks of type 1 are very similar to the hard-burned brick of type 4. (Fig. 8.) The terms, "underburned" and "salmon" as applied to these brick are those used by the manufacturer. They were admittedly unfit for facing purposes and were "draw trials" submitted for experimental tests.

## IV. SUMMARY AND CONCLUSIONS

1. The data indicate that it is possible that differential volume changes may occur between the brick and mortar. A change in temperature alone may cause this. It is indicated, however, that under average climatic conditions, temperature variations would not have so great an effect as variation in the moisture content of the materials.

2. Among the various mortars studied, those which underwent the smallest volume changes during alternate wetting or drying subsequent to hardening, contained only lime and sand.

3. The extent of shrinkage and expansion produced by varying the moisture content was much less in hard-burned (or well-burned)

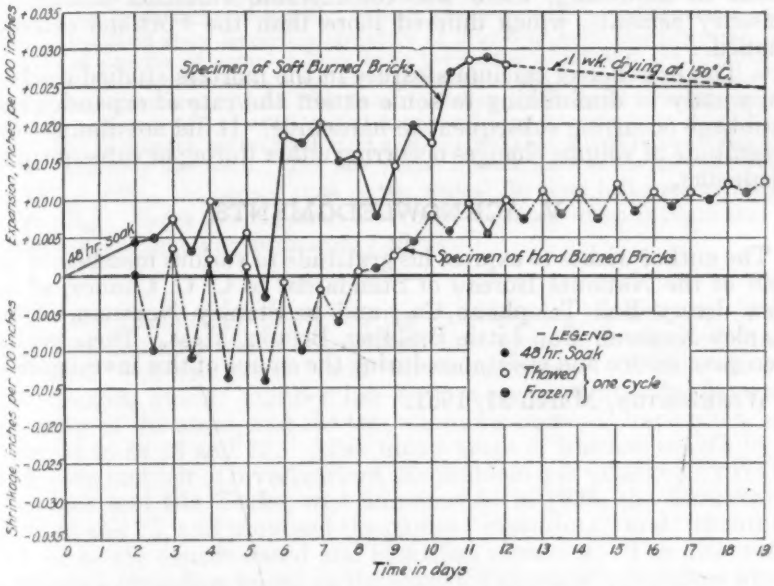


FIGURE 10.—*Linear changes produced by alternately freezing and thawing hard and soft burned bricks (type 7) made from the same clay and molded by the same process*

bricks than in any of the masonry and Portland cement mortars. The difference between lime mortars and bricks is not so great.

4. From the standpoint of volume changes subsequent to hardening, there is less differential volume change if the mortar consists solely of lime and sand. This statement does not apply to masonry containing underburned bricks.

5. It is hardly worth while to use a 1:4 in preference to a 1:3 mortar in brick masonry construction if the shrinkage and expansion alone are considered.

6. The volume changes subsequent to hardening were less in mortar made from 2 volumes of lime to 1 volume of Portland cement to 9 volumes of sand than in mortar made from 1 volume of Portland cement to 3 volumes of sand, using the same cement and sand in both mortars. The data further indicate that from the standpoint of volume changes, there is no distinct advantage in a 1 lime : 1 Portland

cement : 6 sand mortar, using the cements and limes described in this investigation.

7. The initial shrinkage of the lime mortars was greater, in all but one case, than that of the various cement mortars. The exception was masonry cement No. 9. It is believed that the shrinkage of mortars occurring during hardening would be less destructive in masonry than subsequent volume changes, even though the latter are much smaller in magnitude than the former. The possibility of any separation of the unit from the mortar during initial shrinkage would depend on the rate and magnitude of such shrinkage and also on the rate of hardening of the mortar.

8. From the standpoint of volume changes both during and subsequent to hardening, there was considerable variation among the masonry cements, which differed more than the Portland cements studied.

9. The presence of calcium stearate in the mortars studied resulted apparently in diminishing to some extent the rate of expansion and shrinkage occurring subsequent to hardening. It did not diminish the magnitude of volume changes occurring either during or subsequent to hardening.

## V. ACKNOWLEDGMENTS

The author wishes to express his gratitude to various members of the staff of the National Bureau of Standards; to C. C. Connor, of the New Jersey Bell Telephone Co.; and to Stanley Newman, of the Stanley Newman Co., Little Building, Boston, Mass. These gentlemen gave advice and assistance during the course of this investigation.

WASHINGTON, March 21, 1931.

# THE ARC SPECTRUM OF RHENIUM

By William F. Meggers

ABSTRACT

With pure potassium perrhenate on silver electrodes, the arc and spark spectra of rhenium have been photographed from 2,100 A in the ultra-violet to 8,800 A in the infra-red; more than 3,000 new spectral lines have been recorded in this range. Only the lines appearing in the arc spectra with wave lengths exceeding 2,500 A are presented at this time. About 25 per cent of the 2,000 or more lines herein described show hyperfine structure of 2 to 6 or more components. The centers of gravity of complex lines have been determined and are assumed to represent the effective wave lengths for purposes of analyzing the gross structure of the $Re_I$ spectrum. About 500 lines, including all those of intensity greater than 20 on a scale of 1 to 2,000, have been classified as combinations of 115 levels, belonging to quartet, sextet, and octet systems, but only a part of the levels have been completely identified. The raie ultime is recognized as the line at 3,460.47 A, $a^6S_{2½}-e^6P^3_{3½}$, the normal state of the neutral Re atom being represented by $(d^5s^2)\ a^6S_{2½}$. Series forming terms have been identified which indicate that the ionization potential is approximately 7.85 volts.

In 1869 Mendeléev predicted the existence and properties of two chemical elements which should be homologous to manganese; these he called "eka-manganese" and "dvi-manganese." Within the past two decades atomic number has been recognized as a fundamental property of the atom, and the two unknown elements have often been referred to as 43 and 75. After many years of fruitless search by an unknown number of investigators, the problem was attacked by Walter Noddack and Ida Tacke, who announced,[1] in 1925, the discovery of both 43 and 75, and proposed the names "masurium" and "rhenium" for the newly concentrated and identified elements. The discoverers outlined a procedure based on the expected chemical properties whereby the concentrations of these rare elements in certain minerals could be enriched 1,000 fold or more until their presence could be established by the appearance of accurately predictable lines in the Röntgen spectra. Thus the first announcement related to material containing about 0.5 per cent masurium and 5 per cent rhenium, and the proof of their identity was contained in the following table of Röntgen spectra:[2]

| | Masurium 43 | | | Rhenium 75 | | | | |
|---|---|---|---|---|---|---|---|---|
| Line symbol | $K\alpha_1$ | $K\alpha_2$ | $K\beta_1$ | $L\alpha_1$ | $L\alpha_2$ | $L\beta_1$ | $L\beta_2$ | $L\beta_3$ |
| Measured wave length....A.. | 0.672 | 0.675 | 0.601 | 1.4299 | 1.4407 | 1.235 | 1.2048 | 1.216 |
| Calculated wave length....do.. | .6734 | .6779 | .6000 | 1,4306 | 1.4406 | 1.2355 | 1.2041 | 1.2169 |

Apparently little progress has been made in concentrating and purifying masurium, but the rapidity with which the supply of

[1] W. Noddack and I. Tacke, Naturwissenschaften, **13**, p. 567; 1925.
[2] V. Berg and I. Tacke, Naturwissenschaften, **13**, p. 571; 1925.

rhenium, and information concerning its physical and chemical properties, has increased is truly remarkable. In 1927 only 2 mg of rhenium had been concentrated;[3] in 1928 about 120 mg were prepared[4] (at a cost of 30,000 marks), the production of an entire gram of rhenium was described[5] in 1929, while the possibility of an annual production of 120 kg was announced[6] in 1930. Along with the increasing availability of rhenium has come an extensive accumulation of facts as to its chemical and physical properties.[7] In particular, the Röntgen spectra of rhenium have been thoroughly investigated;[8] the wave lengths of 25 L-series lines, 4 M-series lines and 3 L-absorption limits were published by Beuthe in 1928. It is rather surprising, however, that no details concerning the optical emission spectra of rhenium were published until the present writer[9] called attention to some on December 23, 1930. To be sure the discoverers announced,[10] in 1928, that the arc and spark spectra of rhenium were qualitatively known and that several hundred lines were known certainly to belong to rhenium, but no details were given except that the ultimate lines of the optical spectrum, especially the triplet at 3,640 A [11] serve to detect rhenium in concentrations down to $10^{-7}$ and greatly facilitate the examination of rhenium-containing materials.

The optical spectra of rhenium may be expected to be of considerable interest to both practical and theoretical spectroscopists and it was with this point of view that the writer undertook a description and analysis of the spectra when pure material became available. The material used in this investigation was a portion of 1 g of potassium perrhenate ($KReO_4$) kindly presented to this bureau in November, 1930, by Dr. A. v. Grosse, of the Institute of Technology of Berlin. A few crystals of this salt were fused on silver rods in the electric arc, and the spectrum was photographed with a Rowland concave grating mounted stigmatically. The grating has a radius of curvature of 21½ feet and is ruled with 20,000 lines per inch. The entire spectrum from 2,340 to 8,000 A was photographed in the first order spectrum with a scale of 3.7 A per millimeter and a portion (from 2,600 to 4,000 A) was also observed in the second order spectrum with a scale of 1.8 A per millimeter. The observations in the red and infra-red were supplemented and extended to 8,800 A with exposures to a similar spectrograph containing an Anderson ruled

[3] I. Noddack and W. Noddack, Zeit. Angew. Chem., **125**, p. 264; 1927.
[4] I. Noddack and W. Noddack, Zeit. Electrochem., **34**, p. 627; 1928.
[5] I. Noddack and W. Noddack, Zeit. Anorg. Allgem, Chem., **183**, p. 353; 1929.
[6] W. Feit, Zeit. Angew. Chem., **43**, p. 459; 1930.
[7] I. and W. Noddack, Preparation and Some Chemical Properties of Re, Zeit. Angew. Chem., **125**, p. 264; 1927.
W. Noddack, The Chemistry of Rhenium, Zeit. Elektrochemie, **34**, p. 627; 1928.
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I. and W. Noddack, Oxygen Compounds of 75, Naturwissenschaften, **17**, p. 93; 1929.
I. and W. Noddack, New researches on the properties of Rhenium, Forshungen und Fortschritte, **1**, p. 3; 1929.
Agte, Alterthun, Becker, Hyne & Moers, The Physical Properties of Re, Naturwissenschaften, **19**, p. 908; 1931.
[8] O. Berg, The Röntgen Spectrum of 75, Physik. Zeit., **28**, p. 864; 1927.
H. Beuthe, The L-series of Re, Z. Physik., **46**, p. 873; 1928.
I. Wennerlöf, Precision measurements in the L-series of 75, Z. Physik., **47**, p. 422; 1928.
H. Beuthe, Further Röntgen spectroscopy measurements in the L and M series of Re, Z. Physik., **50**, p. 762; 1928.
E. Lindberg, Measurements of the M-series from U (92) to Gd (66), Z. Physik., **56**, p. 82; 1928; **56**, p. 402; 1929.
[9] W. F. Meggers, The Optical Spectra of Rhenium, Phys. Rev., **37**, p. 219, 1931. B. S. Tech. News Bulletin, February, p. 11; 1931.
An anncuncement has recently appeared stating that a list of rhenium wave lengths is being published by Schober and Birke (Naturwissenschaften **19**, p. 211; 1931). Judging from their abbreviated list the values will be on the old Rowland scale.
[10] I. Noddack, Zeit. Elektrochem, **34**, p. 629; 1928.
[11] Probably a typographical error for 3,460.

grating with 7,500 lines per inch giving a scale of 10.4 A per millimeter. A Hilger $E_1$ quartz spectrograph was employed in photographing the Re spectra from 2,500 to 2,100 A, but the spectra are too complex to be satisfactorily described with this instrument. After each arc spectrum exposure the same electrodes were used in a high-voltage spark to record alongside the arc spectrum an exposure of the spark spectrum, thus permitting a sharp division of lines belonging to neutral atoms from those characteristic of ionized atoms. In the list presented here (Table 1) only the lines appearing in the exposure to the 220-volt direct-current arc are given, and some of these are marked E because they appear enhanced in the spark spectrum. Furthermore, only the lines of wave length greater than 2,500 A are being published at the present time because it is planned to reobserve the shorter ones with larger dispersion and higher resolving power so as to obtain satisfactory precision in the wave-length measurements and get some qualitative information as to hyperfine structure comparable with that now available in the visible spectrum. It may be remarked that a very striking feature of the rhenium emission spectra is seen in the complexity of many of its lines. This hyperfine structure is relatively coarse, as might be expected from a heavy odd-numbered atom, and in some cases the components of a line actually cover a wave-number interval of two units. From two to six components have been recognized for different lines, but no systematic effort to resolve hyperfine structures has been attempted thus far. Analysis of the hyperfine structure will be taken up in the immediate future, but for the present we are interested mainly in the gross structure of the spectra. For the purpose in hand the effective wave length of a complex line is regarded as the center of gravity of its unresolved components, and an effort has been made to determine these mean wave lengths with some precision. If the spectrographic resolving power is not too large the image of a complex rhenium line will appear as a narrow rectangle with approximately uniform intensity distribution, and the effective wave length of such a line is taken as the value corresponding to the bisected rectangle in narrow ones or the mean of the opposite edges of wider ones. The spread of the components is indicated qualitatively by letters following the intensity estimate, c signifying complex, cw complex and wider, averaging about one wave number; cW complex and still wider, ranging from one to two wave numbers. In come cases where incipient resolution occurred the unresolved side of the line is indicated by v for violet and l for longer waves. A few lines appearing to be double are marked d.

TABLE 1.—*The arc spectrum of rhenium* ($Re\ I$)

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 2, 500. 59 | 2 | 39, 978. 51 | | 2, 515. 46 | 1 | 39, 742. 20 | |
| 2, 501. 72 | 5 | 39, 960. 46 | | 2, 516. 11 | 15 | 39, 731. 93 | |
| 2, 502, 37 | 3 E | 39, 950. 08 | | 2, 520. 01 | 8 | 39, 670. 45 | 1- 51 |
| 2, 504. 60 | 2 | 39, 914. 51 | | 2, 521. 56 | 5 c | 39, 646. 07 | |
| 2, 505. 41 | 1 | 39, 901. 61 | | 2, 525. 56 | 1 | 39, 583. 28 | |
| 2, 505. 96 | 4 | 39, 892. 85 | | 2, 526. 83 | 1 | 39, 563. 39 | |
| 2, 507. 42 | 3 | 39, 869. 62 | | 2, 529. 50 | 3 | 39, 521. 63 | |
| 2, 508. 98 | 40 | 39, 844. 84 | 1- 52 | 2, 532. 92 | 1 d? | 39, 468. 27 | |
| 2, 512. 55 | 1 | 39, 788. 22 | | 2, 533. 32 | 3 | 39, 462. 04 | |
| 2, 514. 51 | 3 | 39, 757. 21 | | 2, 534. 10 | 1 E | 39, 449. 89 | |

TABLE 1.—*The arc spectrum of rhenium (Re I)*—Continued

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 2,534.80 | 5 c | 39,439.00 | | 2,611.61 | 10 | 38,279.14 | |
| 2,539.33 | 1 | 39,368.64 | | 2,612.76 | 1 | 38,262.29 | |
| 2,540.51 | 4 | 39,350.36 | 2-109 | 2,612.91 | 1 | 38,260.09 | |
| 2,541.09 | 1 h | 39,341.38 | | 2,613.23 | 1 | 38,255.41 | |
| 2,543.68 | 2 | 39,301.33 | | 2,613.76 | 3 | 38,247.65 | |
| 2,543.83 | 1 | 39,299.01 | | 2,614.56 | 5 | 38,235.95 | |
| 2,544.22 | 2 | 29,292.98 | | 2,615.70 | 1 E | 38,219.29 | |
| 2,544.75 | 10 | 39,284.80 | | 2,616.72 | 1 E | 38,204.39 | |
| 2,544.89 | 2 | 39,282.64 | | 2,617.14 | 2 | 38,198.26 | |
| 2,545.49 | 5 | 39,273.38 | | 2,617.47 | 2 | 38,193.44 | |
| 2,548.13 | 2 | 39,232.70 | | 2,620.04 | 4 | 38,155.98 | |
| 2,548.89 | 3 | 39,221.00 | | 2,620.36 | 3 | 38,151.32 | |
| 2,550.09 | 1 E | 39,202.54 | | 2,621.18 | 2 | 38,139.39 | |
| 2,552.02 | 4 | 39,172.90 | | 2,621.99 | 2 | 38,127.60 | |
| 2,552.70 | 1 | 39,162.46 | | 2,622.77 | 5 | 38,116.26 | |
| 2,553.57 | 1 E | 39,149.12 | | 2,623.30 | 2 | 38,108.57 | |
| 2,554.18 | 2 | 39,139.77 | | 2,625.05 | 1 | 38,083.16 | |
| 2,554.63 | 2 E | 39,132.88 | | 2,625.82 | 1 | 38,072.00 | |
| 2,554.94 | 1 | 39,128.13 | | 2,630.17 | 1 | 38,009.03 | |
| 2,555.66 | 1 | 39,117.11 | | 2,630.77 | 2 | 38,000.36 | |
| 2,556.50 | 20 | 39,104.26 | | 2,631.59 | 3 | 37,988.53 | |
| 2,558.05 | 2 | 39,080.56 | | 2,633.02 | 1 | 37,967.90 | |
| 2,559.07 | 5 | 39,064.99 | 1-47 | 2,633.63 | 3 | 37,959.10 | |
| 2,559.74 | 2 | 39,054.77 | | 2,635.84 | 2 E | 37,927.28 | |
| 2,559.88 | 1 | 39,052.63 | | 2,636.64 | 20 | 37,915.77 | 1-41 |
| 2,561.46 | 2 | 39,028.54 | | 2,637.00 | 2 E | 37,910.60 | |
| 2,563.01 | 2 | 39,004.94 | | 2,641.02 | 1 E | 37,852.90 | |
| 2,564.19 | 4 | 38,986.99 | | 2,641.18 | 1 | 37,850.60 | |
| 2,565.84 | 1 | 38,961.92 | | 2,642.76 | 8 | 37,827.98 | |
| 2,568.65 | 3 E | 38,919.30 | | 2,644.77 | 1 | 37,799.23 | |
| 2,571.26 | 3 | 38,879.80 | | 2,645.81 | 1 | 37,784.37 | |
| 2,571.82 | 2 E | 38,871.33 | | 2,646.40 | 1 | 37,775.95 | |
| 2,573.78 | 3 | 38,841.73 | | 2,647.14 | 6 | 37,765.39 | 1-40 |
| 2,574.22 | 1 | 38,835.10 | | 2,648.49 | 1 E | 37,746.14 | |
| 2,576.33 | 2 | 38,803.29 | | 2,649.06 | 7 | 37,738.02 | |
| 2,578.14 | 1 | 38,776.05 | | 2,649.58 | 2 | 37,730.61 | |
| 2,579.02 | 3 | 38,762.82 | | 2,651.90 | 20 | 37,697.60 | 1-39 |
| 2,580.31 | 1 | 38,743.44 | | 2,652.92 | 3 | 37,683.11 | |
| 2,581.43 | 3 | 38,726.64 | | 2,653.74 | 1 | 37,671.47 | |
| 2,582.79 | 2 | 38,706.24 | | 2,654.12 | 7 | 37,666.08 | |
| 2,584.77 | 2 | 38,676.60 | | 2,655.18 | 2 | 37,651.04 | |
| 2,586.80 | 10 | 38,646.25 | | 2,655.84 | 2 | 37,641.68 | |
| 2,587.02 | 1 | 38,642.96 | | 2,657.45 | 1 | 37,618.88 | |
| 2,587.18 | 1 | 38,640.57 | | 2,658.69 | 1 | 37,601.34 | |
| 2,591.14 | 2 | 38,581.52 | | 2,659.02 | 2 | 37,596.67 | |
| 2,591.47 | 1 | 38,576.61 | | 2,659.79 | 2 | 37,585.79 | |
| 2,591.60 | 3 | 38,574.68 | | 2,660.56 | 1 h | 37,574.91 | |
| 2,592.85 | 2 c? | 38,556.08 | | 2,661.02 | 1 | 37,568.41 | |
| 2,594.86 | 4 | 38,526.22 | 2-103 | 2,663.63 | 8 | 37,531.61 | |
| 2,595.24 | 7 | 38,520.58 | 1-44 | 2,664.21 | 2 | 37,523.43 | |
| 2,596.42 | 2 | 38,503.07 | | 2,664.80 | 2 | 37,515.13 | |
| 2,596.79 | 3 | 38,497.58 | | 2,667.13 | 2 | 37,482.35 | |
| 2,596.96 | 2 | 38,495.06 | | 2,667.79 | 1 | 37,473.08 | |
| 2,597.98 | 1 | 38,479.95 | | 2,670.23 | 3 | 37,438.84 | 2-100 |
| 2,598.60 | 1 | 38,470.77 | | 2,670.80 | 3 | 37,430.85 | |
| 2,599.86 | 8 | 38,452.13 | | 2,671.84 | 4 | 37,416.28 | |
| 2,600.87 | 1 | 38,437.19 | | 2,672.77 | 2 | 37,403.27 | |
| 2,601.89 | 2 | 38,422.13 | | 2,674.33 | 40 | 37,381.45 | 1-38 |
| 2,602.55 | 1 | 38,412.39 | | 2,677.04 | 3 | 37,343.61 | |
| 2,602.93 | 2 | 38,406.78 | | 2,677.77 | 2 | 37,333.43 | |
| 2,603.47 | 2 | 38,398.81 | | 2,679.09 | 2 | 37,315.04 | |
| 2,603.88 | 6 c? | 38,392.77 | | 2,679.92 | 4 | 37,303.48 | |
| 2,607.32 | 1 | 38,342.12 | | 2,681.02 | 1 | 37,288.18 | |
| 2,608.51 | 4 E | 38,324.63 | | 2,683.56 | 4 | 37,252.88 | |
| 2,609.41 | 1 | 38,311.41 | | 2,685.30 | 2 | 37,228.75 | |

TABLE 1.—*The arc spectrum of rhenium (Re I)*—Continued

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 2,688.53 | 8 | 37,184.02 | | 2,768.86 | 4 | 36,105.30 | 3–94 |
| 2,689.34 | 2 | 37,172.82 | | 2,769.33 | 3 c | 36,099.18 | |
| 2,690.26 | 4 | 37,160.11 | | 2,770.41 | 10 | 36,085.11 | 2–93 |
| 2,690.79 | 3 | 37,152.80 | | 2,771.62 | 1 | 36,069.35 | |
| 2,693.76 | 1 h | 37,111.84 | | 2,772.42 | 1 | 36,058.95 | |
| 2,694.40 | 3 | 37,103.02 | | 2,773.12 | 4 | 36,049.84 | |
| 2,695.56 | 4 | 37,087.05 | | 2,774.39 | 1 | 36,033.34 | |
| 2,697.27 | 4 | 37,063.54 | 1–37 | 2,775.64 | 2 | 36,017.12 | |
| 2,698.79 | 1 | 37,042.67 | | 2,775.94 | 1 | 36,013.22 | |
| 2,699.58 | 1 | 37,031.83 | | 2,776.95 | 1 | 36,000.12 | |
| 2,702.68 | 2 | 36,989.36 | | 2,777.22 | 1 | 35,996.63 | |
| 2,703.28 | 1 | 36,981.15 | | 2,777.73 | 2 | 35,990.02 | |
| 2,704.39 | 4 | 36,965.97 | | 2,778.09 | 2 | 35,985.35 | |
| 2,706.06 | 1 | 36,943.16 | | 2,778.50 | 2 | 35,980.04 | |
| 2,706.50 | 1 | 36,937.15 | | 2,779.31 | 1 | 35,969.56 | |
| 2,707.40 | 1 | 36,924.87 | | 2,780.80 | 1 h | 35,950.29 | |
| 2,707.84 | 1 | 36,918.88 | | 2,781.44 | 4 | 35,942.02 | |
| 2,710.23 | 1 | 36,886.32 | | 2,783.16 | 1 | 35,919.81 | |
| 2,712.49 | 2 | 36,855.59 | | 2,783.57 | 12 c | 35,914.51 | 3–93 |
| 2,713.04 | 3 | 36,848.12 | | 2,785.20 | 4 | 35,893.50 | 6–103 |
| 2,713.17 | 2 | 36,846.35 | | 2,785.43 | 2 | 35,890.53 | |
| 2,713.68 | 1 | 36,839.43 | | 2,785.72 | 2 | 35,886.80 | |
| 2,715.47 | 40 | 36,815.14 | 3–99 | 2,786.14 | 2 | 35,881.39 | |
| 2,715.78 | 4 | 36,810.94 | | 2,786.55 | 4 | 35,876.11 | 9–109 |
| 2,716.77 | 3 | 36,797.53 | | 2,787.41 | 1 | 35,865.04 | |
| 2,719.55 | 2 | 36,759.92 | | 2,789.26 | 3 d | 35,841.26 | |
| 2,720.66 | 1 | 36,744.92 | | 2,790.94 | 4 | 35,819.68 | |
| 2,722.21 | 4 | 36,724.00 | | 2,791.29 | 8 | 35,815.19 | |
| 2,722.72 | 6 | 36,717.12 | 6–109 | 2,791.60 | 1 | 35,811.21 | |
| 2,723.36 | 1 | 36,708.49 | | 2,793.68 | 1 | 35,784.55 | |
| 2,723.86 | 1 | 36,701.75 | | 2,794.16 | 1 | 35,778.40 | |
| 2,727.55 | 3 | 36,652.11 | | 2,796.07 | 1 | 35,753.97 | |
| 2,728.63 | 2 | 36,637.60 | | 2,796.60 | 1 | 35,747.19 | |
| 2,729.65 | 2 | 36,623.91 | | 2,797.45 | 1 | 35,736.33 | |
| 2,730.84 | 2 | 36,607.95 | | 2,798.11 | 3 | 35,727.90 | |
| 2,731.56 | 3 c E | 36,598.30 | | 2,800.70 | 7 c | 35,694.86 | |
| 2,732.21 | 8 | 36,589.60 | | 2,802.25 | 4 | 35,675.12 | |
| 2,733.04 | 6 E | 36,578.48 | | 2,802.83 | 1 | 35,667.74 | |
| 2,734.32 | 2 | 36,561.36 | | 2,803.26 | 4 E | 35,662.27 | |
| 2,734.90 | 2 | 36,553.61 | | 2,805.98 | 1 | 35,627.70 | |
| 2,738.33 | 3 | 36,507.83 | | 2,807.87 | 3 c | 35,603.72 | |
| 2,738.73 | 1 d | 36,502.49 | | 2,812.07 | 2 | 35,550.55 | |
| 2,739.97 | 2 | 36,485.98 | | 2,812.37 | 3 | 35,546.75 | |
| 2,741.98 | 1 | 36,459.23 | | 2,813.12 | 2 | 35,537.28 | |
| 2,742.78 | 1 | 36,448.60 | | 2,813.96 | 5 | 35,526.67 | |
| 2,742.86 | 2 | 36,447.53 | | 2,814.67 | 10 | 35,517.79 | |
| 2,743.88 | 3 | 36,433.98 | | 2,815.64 | 1 | 35,505.47 | |
| 2,744.21 | 1 | 36,429.60 | 3–98 | 2,816.33 | 4 | 35,496.77 | |
| 2,745.87 | 2 | 36,407.58 | | 2,816.96 | 4 | 35,488.84 | 8–103 |
| 2,747.43 | 4 | 36,386.91 | 2–97 | 2,819.95 | 30 cw | 35,451.21 | 3–92 |
| 2,752.88 | 3 | 36,314.88 | | 2,822.12 | 3 | 35,423.95 | |
| 2,753.06 | 4 | 36,312.50 | 8–109 | 2,822.42 | 1 | 35,420.19 | 2–91 |
| 2,753.66 | 1 h E | 36,304.59 | | 2,823.21 | 3 | 35,410.27 | |
| 2,755.22 | 2 | 36,284.04 | 5–103 | 2,823.88 | 1 E | 35,401.88 | |
| 2,757.50 | 2 | 36,254.04 | | 2,824.25 | 3 | 35,397.24 | |
| 2,758.02 | 8 | 36,247.20 | | 2,825.46 | 2 E | 35,382.08 | |
| 2,758.72 | 2 | 36,238.01 | | 2,826.77 | 1 h | 35,365.68 | |
| 2,761.93 | 3 | 36,195.89 | | 2,827.52 | 3 | 35,356.30 | |
| 2,763.31 | 2 | 36,177.82 | 3–96 | 2,827.83 | 1 | 35,352.43 | |
| 2,763.79 | 4 | 36,171.53 | | 2,829.88 | 1 | 35,326.82 | |
| 2,766.06 | 1 | 36,141.85 | | 2,830.10 | 1 | 35,324.07 | |
| 2,766.40 | 2 c | 36,137.41 | | 2,830.82 | 1 | 35,315.09 | |
| 2,766.54 | 1 | 36,135.58 | | 2,834.08 | 10 c | 35,274.47 | |
| 2,767.75 | 8 | 36,119.79 | | 2,834.62 | 2 | 35,267.75 | 1–34 |
| 2,768.28 | 1 | 36,112.87 | | 2,836.69 | 1 | 35,242.01 | |

TABLE 1.—*The arc spectrum of rhenium (Re I)*—Continued

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 2,837.01 | 1 | 35,238.04 | | 2,913.81 | 1 | 35,309.31 | |
| 2,837.54 | 6 | 35,231.46 | | 2,915.27 | 1 | 35,292.12 | |
| 2,838.10 | 1 | 35,224.51 | | 2,916.29 | 1 h | 35,280.13 | |
| 2,839.18 | 1 | 35,211.11 | | 2,916.80 | 1 d | 35,274.14 | |
| 2,840.35 | 7 | 35,196.60 | 5–100 | 2,918.87 | 2 | 35,249.83 | |
| 2,842.99 | 7 | 35,163.92 | 10–109 | 2,919.41 | 84 | 34,243.50 | |
| 2,844.16 | 3 | 35,149.46 | | 2,921.71 | 1 | 34,216.54 | |
| 2,846.48 | 1 | 35,120.81 | | 2,924.60 | 6 cw | 34,182.73 | 3–84 |
| 2,846.97 | 3 | 35,114.76 | | 2,925.19 | 3 | 34,175.84 | |
| 2,847.73 | 1 | 35,105.39 | | 2,926.94 | 2 | 34,155.40 | |
| 2,848.23 | 2 d | 35,099.23 | | 2,927.42 | 20 cw | 34,149.81 | |
| 2,850.28 | 1 | 35,073.99 | | 2,927.70 | 1 | 34,146.54 | |
| 2,850.97 | 10 | 35,065.50 | 2–90 | 2,928.58 | 1 | 34,136.28 | |
| 2,852.38 | 1 | 35,048.17 | | 2,929.53 | 5 | 34,125.21 | |
| 2,852.85 | 3 | 35,042.40 | | 2,930.60 | 7 | 34,112.75 | |
| 2,855.52 | 2 | 35,009.63 | | 2,931.67 | 1 | 34,100.30 | |
| 2,857.44 | 2 | 34,986.11 | | 2,932.28 | 2 d | 34,093.21 | |
| 2,860.08 | 2 | 34,953.82 | | 2,933.44 | 1 | 34,079.73 | |
| 2,860.26 | 2 | 34,951.62 | | 2,934.01 | 1 | 34,073.11 | 5–95 |
| 2,862.18 | 1 | 34,928.17 | | 2,936.50 | 3 | 34,044.22 | |
| 2,862.88 | 2 | 34,919.63 | | 2,937.83 | 1 | 34,028.80 | |
| 2,864.57 | 2 | 34,899.03 | | 2,938.80 | 1 | 34,017.57 | |
| 2,864.81 | 1 | 34,896.11 | | 2,940.99 | 1 E | 33,992.24 | |
| 2,867.20 | 8 | 34,867.02 | | 2,941.56 | 2 | 33,985.66 | |
| 2,868.14 | 1 | 34,855.59 | | 2,943.14 | 10 | 33,967.41 | 6–98 |
| 2,871.81 | 6 | 34,811.05 | 6–101 | 2,943.39 | 2+E? | 33,964.53 | 9–109 |
| 2,872.29 | 2 | 34,805.24 | | 2,944.34 | 2 | 33,953.57 | |
| 2,872.67 | 1 | 34,800.63 | | 2,945.70 | 2 | 33,937.89 | |
| 2,875.28 | 6 | 34,769.04 | 2–87 | 2,945.88 | 1 | 33,935.82 | |
| 2,876.03 | 1 | 34,759.98 | | 2,946.57 | 2 | 33,927.87 | |
| 2,876.87 | 2 | 34,749.83 | | 2,949.10 | 3 | 33,898.77 | |
| 2,879.28 | 2 | 34,720.74 | | 2,949.26 | 1 | 33,896.93 | |
| 2,881.88 | 1 E | 34,689.42 | | 2,949.89 | 2 | 33,889.69 | 4–86 |
| 2,882.23 | 1 | 34,685.21 | | 2,950.84 | 4 | 33,878.78 | 2–83 |
| 2,883.45 | 6 | 34,670.53 | | 2,954.34 | 3 | 33,838.65 | |
| 2,884.04 | 2 | 34,663.44 | | 2,954.62 | 1 d | 33,835.44 | |
| 2,884.64 | 3 | 34,656.23 | | 2,957.90 | 1 c E | 33,797.92 | |
| 2,885.17 | 1 d | 34,649.87 | | 2,958.92 | 2 | 33,786.27 | |
| 2,885.93 | 1 | 34,640.74 | | 2,959.32 | 1 | 33,781.70 | |
| 2,886.95 | 2 | 34,628.50 | | 2,959.77 | 1 | 33,776.57 | |
| 2,887.35 | 2 | 34,623.71 | | 2,960.29 | 1 | 33,770.64 | |
| 2,887.67 | 60 | 34,619.87 | 3–88 | 2,961.76 | 3 c | 33,753.88 | 6–97 |
| 2,888.04 | 2 E | 34,615.43 | | 2,962.27 | 8 | 33,748.06 | |
| 2,889.45 | 3 | 34,598.54 | 3–87 | 2,962.86 | 2 | 33,741.34 | |
| 2,891.48 | 3 | 34,574.25 | | 2,965.12 | 20 c | 33,715.63 | 6–96 |
| 2,891.88 | 6 | 34,569.47 | | 2,965.75 | 40 cw | 33,708.47 | 3–83 |
| 2,892.63 | 4 | 34,560.51 | | 2,967.25 | 3 | 33,691.43 | |
| 2,894.32 | 3 | 34,540.33 | | 2,968.05 | 5 | 33,682.35 | 6–95 |
| 2,895.67 | 2 | 34,524.23 | | 2,968.97 | 2 | 33,671.91 | |
| 2,896.00 | 20 cw | 34,520.30 | 1–31 | 2,975.04 | 2 | 33,603.21 | 15–109 |
| 2,896.44 | 1 | 34,515.05 | | 2,975.25 | 3 | 33,600.84 | |
| 2,897.59 | 2 | 34,501.35 | | 2,976.29 | 10 c | 33,589.10 | {1–28 {3–82 |
| 2,898.79 | 2 | 34,487.07 | | 2,977.30 | 2 | 33,577.71 | |
| 2,902.50 | 20 cW | 34,442.99 | 17–11b | 2,978.15 | 5 | 33,568.12 | |
| 2,904.53 | 1 E | 34,418.92 | | 2,980.29 | 1 | 33,544.02 | |
| 2,905.42 | 2 | 35,408.38 | | 2,980.84 | 5 | 33,537.83 | |
| 2,905.58 | 6 | 35,406.49 | 8–101 | 2,980.99 | 2 | 33,536.15 | |
| 2,906.01 | 5 | 35,401.39 | 8–100 | 2,982.19 | 5 c | 33,522.65 | |
| 2,907.10 | 2 | 35,388.50 | | 2,984.52 | 1 | 33,496.48 | |
| 2,908.34 | 3 | 35,373.83 | | 2,984.75 | 2 | 33,493.90 | |
| 2,909.81 | 15 | 35,356.47 | | 2,986.04 | 2 | 33,479.43 | |
| 2,910.08 | 2 | 35,353.28 | 2–84 | 2,988.48 | 6 | 33,452.10 | 6–93 |
| 2,911.23 | 2 | 35,339.71 | 10–103 | 2,991.86 | 1 | 33,414.31 | |
| 2,912.59 | 1 | 35,323.68 | | 2,992.36 | 50 | 33,408.72 | 1–26 |
| 2,913.15 | 2 | 35,317.08 | | 2,992.80 | 2 c | 33,403.81 | |

TABLE 1.—*The arc spectrum of rhenium* ($Re_I$)—Continued

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 2,993.18 | 2 | 33,399.57 | | 3,065.58 | 2 | 32,610.81 | 9- 93 |
| 2,995.39 | 3 | 33,374.93 | | 3,067.39 | 50 | 32,591.56 | 1- 25 |
| 2,997.70 | 1 | 33,349.21 | 8- 97 | 3,068.76 | 2 | 32,577.01 | |
| 2,998.55 | 1 | 33,339.76 | | 3,069.94 | 10 | 32,564.49 | |
| 2,999.58 | 80 | 33,328.31 | 3- 81 | 3,071.16 | 6 | 32,551.56 | |
| 3,000.59 | 1 | 33,317.09 | | 3,071.76 | 3 hl | 32,545.20 | |
| 3,001.13 | 8 | 33,311.10 | | 3,072.45 | 1 | 32,537.89 | |
| 3,004.13 | 7 | 33,277.84 | 8- 95 | 3,072.96 | 6 | 32,532.49 | |
| 2,004.34 | 2 | 33,275.51 | | 3,075.02 | 2 h | 32,510.70 | |
| 3,005.23 | 1 | 33,265.66 | | 3,076.14 | 3 | 32,498.86 | |
| 3,005.96 | 3 | 33,257.58 | 10-101 | 3,076.28 | 1 | 32,497.38 | |
| 2,006.43 | 7 | 33,252.38 | 10-100 | 3,078.87 | 4 | 32,470.05 | 3- 76 |
| 3,007.04 | 2 | 33,245.63 | | 3,080.92 | 2 | 32,448.44 | |
| 3,007.19 | 2 | 33,243.98 | | 3,081.63 | 1 | 32,440.97 | |
| 3,010.64 | 1 | 33,205.88 | | 3,082.43 | 20 cw v | 32,432.55 | 6- 90 |
| 3,011.47 | 1 | 33,196.73 | | 3,082.76 | 1 | 32,429.08 | |
| 3,011.94 | 4 cw | 33,191.55 | | 3,084.21 | 4 c | 32,413.83 | 10- 98 |
| 3,013.15 | 6 | 33,178.22 | 5- 91 | 3,084.79 | 2 | 32,407.74 | |
| 3,014.95 | 1 | 33,158.41 | | 3,085.36 | 1 | 32,401.75 | |
| 3,016.02 | 20 cw v | 33,146.65 | 3- 79 | 3,085.54 | 1 | 32,399.86 | |
| 3,016.48 | 10 | 33,141.60 | | 3,087.16 | 3 | 32,382.86 | 8- 91 |
| 3,016.96 | 2 | 33,136.32 | | 3,088.76 | 10 | 32,366.08 | |
| 3,017.27 | 1 | 33,132.92 | | 3,089.93 | 2 | 32,353.83 | |
| 3,017.59 | 1 | 33,129.40 | | 3,092.33 | 1 | 32,328.72 | |
| 3,021.88 | 6 | 33,082.38 | | 3,093.64 | 6 c | 32,315.03 | 5- 86 |
| 3,022.99 | 3 | 33,070.23 | | 3,095.06 | 4 | 32,300.20 | |
| 3,023.59 | 1 | 33,063.67 | | 3,095.80 | 6 cw | 32,292.48 | 6- 89 |
| 3,025.05 | 2 | 33,047.71 | 8- 93 | 3,096.41 | 3 | 32,286.12 | 5- 85 |
| 3,026.26 | 2 | 33,034.50 | | 3,097.93 | 1 | 32,270.28 | |
| 3,030.44 | 15 c | 32,988.93 | 6- 92 | 3,098.27 | 1 | 32,266.74 | |
| 3,031.26 | 2 | 32,980.01 | | 3,099.70 | 1 c | 32,251.86 | |
| 3,032.79 | 3 | 32,963.37 | | 3,100.66 | 20 | 32,241.87 | 12-99? |
| 3,034.53 | 5 | 32,944.47 | 18-115 | 3,101.00 | 1 | 32,238.34 | |
| 3,035.61 | 2 | 32,932.75 | | 3,101.71 | 1 | 32,230.96 | |
| 3,036.55 | 3 | 32,922.56 | | 3,103.08 | 2 E | 32,216.73 | |
| 3,037.44 | 1 | 32,912.91 | 9- 97 | 3,103.26 | 2 c E | 32,214.86 | |
| 3,037.95 | 4 | 32,907.39 | | 3,104.65 | 4 | 32,200.44 | 10- 97 |
| 3,040.04 | 5 cw | 32,884.76 | | 3,107.86 | 1 d | 32,167.18 | |
| 3,041.00 | 3 | 32,874.38 | 9- 96 | 3,108.80 | 40 | 32,157.45 | 6- 88 |
| 3,041.24 | 1 | 32,871.79 | | 3,109.75 | 2 | 32,147.63 | 9- 92 |
| 3,041.76 | 1 | 32,866.17 | | 3,110.86 | 12 | 32,136.16 | 6- 87 |
| 3,041.99 | 2 | 32,863.68 | | 3,111.57 | 3 | 32,128.83 | 10- 95 |
| 3,042.29 | 2 | 32,860.44 | | 3,113.21 | 2 | 32,111.90 | |
| 3,044.08 | 3 | 32,841.12 | 9- 95 | 3,113.97 | 1 | 32,104.07 | |
| 3,045.28 | 1 | 32,828.18 | | 3,114.62 | 1 | 32,097.37 | |
| 3,046.00 | 1 | 32,820.42 | | 3,118.20 | 20 cW v | 32,060.52 | |
| 3,047.26 | 6 c? | 32,806.85 | | 3,119.22 | 2 | 32,050.03 | |
| 3,048.58 | 1 | 32,792.65 | | 3,119.85 | 1 | 32,043.56 | |
| 3,049.79 | 2 | 32,779.64 | 15-103 | 3,120.24 | 1 | 32,039.56 | |
| 3,051.60 | 1 | 32,760.20 | | 3,121.37 | 12 c | 32,027.96 | 8- 90 |
| 3,052.24 | 1 | 32,753.33 | | 3,121.73 | 1 | 32,024.26 | |
| 3,052.84 | 2 c? | 32,746.89 | | 3,122.22 | 1 | 32,019.24 | |
| 3,053.62 | 3 | 32,738.52 | | 3,123.17 | 3 | 32,009.50 | |
| 3,054.90 | 4 | 32,724.81 | 2- 77 | 3,123.40 | 1 | 32,007.14 | |
| 3,056.00 | 2 c | 32,713.03 | | 3,125.35 | 1 h | 31,987.17 | |
| 3,056.45 | 1 | 32,708.21 | | 3,125.52 | 3 | 31,985.43 | 2- 72 |
| 3,057.66 | 3 | 32,695.27 | 12-100 | 3,126.03 | 1 | 31,980.22 | |
| 3,057.86 | 2 | 32,693.13 | | 3,128.94 | 15 cw | 31,950.47 | 13- 99 |
| 3,058.78 | 7 | 32,683.30 | 5- 89 | 3,131.27 | 1 h | 31,926.70 | |
| 3,060.32 | 3 | 32,666.85 | | 3,132.03 | 2 h | 31,918.95 | 7- 87 |
| 3,061.21 | 1 | 32,657.36 | | 3,134.02 | 6 | 31,898.69 | 10- 93 |
| 3,061.61 | 3 | 32,653.09 | | 3,134.34 | 1 | 31,895.43 | 6- 85 |
| 3,062.50 | 1 | 32,643.60 | | 3,135.07 | 3 c | 31,888.00 | 8- 89 |
| 3,064.61 | 2 | 32,621.13 | | 3,138.02 | 1 | 31,858.03 | |
| 3,065.28 | 2 | 32,614.00 | | 3,139.80 | 3 c | 31,839.97 | |

TABLE 1.—*The arc spectrum of rhenium (Re I)*—Continued

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 3,139.94 | 2 | 31,838.55 | | 3,208.23 | 2 | 31,160.86 | |
| 3,141.37 | 7 | 31,824.06 | 2- 69 | 3,211.75 | 4 c | 31,126.71 | 6- 82 |
| 3,141.71 | 1 | 31,820.61 | | 3,212.38 | 1 | 31,120.61 | |
| 3,142.63 | 5 c | 31,811.30 | | 3,212.94 | 3 cw | 31,115.18 | |
| 3,145.58 | 1 | 31,781.46 | | 3,213.48 | 2 | 31,109.95 | |
| 3,146.53 | 2 | 31,771.87 | | 3,213.90 | 1 | 31,105.89 | |
| 3,147.70 | 1 | 31,760.06 | | 3,214.11 | 2 | 31,103.86 | |
| 3,147.89 | 1 | 31,758.14 | 2- 68 | 3,214.82 | 1 | 31,096.99 | |
| 3,148.20 | 2 | 31,755.02 | | 3,219.74 | 1 | 31,049.47 | |
| 3,150.05 | 1 | 31,736.37 | | 3,219.92 | 2 E | 31,047.74 | |
| 3,150.53 | 1 | 31,731.53 | 8- 87 | 3,220.45 | 1 | 31,042.63 | |
| 3,151.16 | 2 | 31,725.19 | | 3,221.17 | 1 | 31,035.69 | |
| 3,151.63 | 15 cw | 31,720.46 | 6- 84 | 3,221.84 | 1 E | 31,029.23 | |
| 3,153.77 | 10 | 31,698.94 | 3- 71 | 3,224.23 | 1 | 31,006.23 | |
| 3,156.84 | 1 | 31,668.11 | | 3,227.46 | 4 | 30,975.20 | |
| 3,157.70 | 1 | 31,659.48 | | 3,228.36 | 1 c | 30,966.57 | |
| 3,158.31 | 25 cWv | 31,653.37 | 3- 69 | 3,228.74 | 3 | 30,962.93 | |
| 3,159.30 | 2 | 31,643.45 | 12- 97 | 3,235.95 | 10 | 30,893.94 | |
| 3,159.61 | 1 h | 31,640.35 | | 3,237.00 | 1 h | 30,883.92 | |
| 3,160.19 | 2 h | 31,634.54 | | 3,237.52 | 4 | 30,878.96 | 9- 84<br>10- 90 |
| 3,162.48 | 2 d? | 31,611.63 | | | | | |
| 3,163.23 | 1 | 31,604.14 | | 3,238.36 | 1 | 30,870.95 | |
| 3,164.13 | 1 | 31,595.15 | | 3,239.17 | 2 | 30,863.23 | |
| 3,164.51 | 6 | 31,591.36 | 9- 90 | 3,241.47 | 3 | 30,841.33 | 8- 83 |
| 3,164.85 | 2 | 31,587.96 | | 3,246.32 | 2 E | 30,795.26 | |
| | | | | 3,248.55 | 3 | 30,774.12 | |
| 3,165.79 | 2 | 31,578.58 | | | | | |
| 3,166.47 | 2 | 31,571.80 | 12- 95 | 3,252.26 | 4 | 30,739.01 | 10- 89 |
| 3,166.91 | 2 | 31,567.41 | | 3,253.18 | 2 c? | 30,730.32 | |
| 3,167.15 | 3 | 31,565.02 | 13- 98 | 3,253.95 | 3 cw | 30,723.05 | |
| 3,167.59 | 1 | 31,560.64 | | 3,255.80 | 1 | 30,705.59 | |
| | | | | 3,256.29 | 2 | 30,700.97 | |
| 3,168.36 | 30 cw | 31,552.97 | 11- 94 | | | | |
| 3,170.98 | 2 c | 31,526.90 | | 3,258.07 | 1 | 30,684.20 | 6- 79 |
| 3,173.09 | 3 | 31,505.94 | | 3,258.85 | 15 | 30,676.86 | 12- 91 |
| 3,174.61 | 6 | 31,490.85 | 8- 85 | 3,259.55 | 20 | 30,670.27 | |
| 3,174.77 | 4 cw | 31,489.27 | | 3,261.56 | 4 c? | 30,651.37 | |
| | | | | 3,262.77 | 3 | 30,640.00 | 15- 97 |
| 3,176.06 | 1 | 31,476.48 | | | | | |
| 3,177.71 | 15 | 31,460.13 | | 3,266.85 | 3 c | 30,601.73 | 15- 96 |
| 3,178.49 | 2 | 31,452.41 | | 3,268.09 | 3 c | 30,590.12 | |
| 3,178.60 | 5 | 31,451.32 | 9- 89 | 3,268.49 | 5 | 30,586.38 | 13- 92 |
| 3,180.88 | 1 | 31,428.78 | | 3,268.90 | 4 c | 30,582.54 | 10- 87 |
| | | | | 3,269.04 | 3 c | 30,581.24 | |
| 3,182.70 | 3 | 31,410.81 | | | | | |
| 3,182.87 | 25 c | 31,409.14 | 17-106 | 3,270.04 | 1 | 30,571.88 | |
| 3,184.75 | 50 c | 31,390.59 | 17-105 | 3,271.09 | 1 | 30,562.07 | |
| 3,185.56 | 40 c | 31,382.61 | 17-104 | 3,277.73 | 3 c? | 30,500.16 | |
| 3,186.28 | 3 | 31,375.52 | | 3,285.67 | 2 | 30,426.46 | |
| | | | | 3,287.12 | 2 | 30,413.04 | |
| 3,187.78 | 2 | 31,360.76 | | | | | |
| 3,190.17 | 4 | 31,337.26 | | 3,290.10 | 1 | 30,385.49 | 3- 65 |
| 3,190.78 | 6 | 31,331.27 | 14- 99 | 3,294.82 | 4 | 30,341.96 | 10- 85 |
| 3,192.36 | 6 c | 31,315.76 | 8- 84 | 3,296.70 | 6 c | 30,324.66 | 17-102 |
| 3,192.68 | 1 | 31,312.63 | | 3,296.98 | 6 c v | 30,322.06 | 12- 90 |
| | | | | 3,300.97 | 2 | 30,285.43 | 9- 82 |
| 3,193.19 | 3 | 31,307.62 | | | | | |
| 3,194.49 | 7 cw | 31,294.88 | 9- 87 | 3,301.59 | 5 | 30,279.75 | 8- 79 |
| 3,195.66 | 1 | 31,283.43 | | 3,302.22 | 4 | 30,273.97 | |
| 3,197.24 | 1 | 31,267.97 | | 3,303.21 | 5 cWE | 30,264.90 | |
| 3,197.52 | 1 | 31,265.23 | | 3,303.75 | 7 | 30,259.95 | 2- 64 |
| | | | | 3,304.85 | 1 | 30,249.88 | |
| 3,198.57 | 6 | 31,254.97 | | | | | |
| 3,199.50 | 2 | 31,245.88 | 6- 83 | 3,306.50 | 1 | 30,234.79 | |
| 3,200.03 | 5 cw | 31,240.71 | 13- 94 | 3,307.00 | 3 c | 30,230.22 | |
| 3,200.72 | 3 | 31,233.97 | 10- 91 | 3,308.25 | 3 | 30,218.79 | |
| 3,202.22 | 2 | 31,219.34 | | 3,308.46 | 3 cWE | 30,216.88 | |
| | | | | 3,308.87 | 2 | 30,213.13 | |
| 3,204.24 | 60 cWl | 31,199.66 | | 3,309.31 | 2 | 30,209.12 | |
| 3,204.68 | 1 | 31,195.38 | | 3,312.30 | 3 | 30,181.84 | 12- 89 |
| 3,205.42 | 3 c | 31,188.18 | | 3,313.95 | 6 | 30,166.82 | 10- 84 |
| 3,206.47 | 2 | 31,177.97 | | 3,316.07 | 1 | 30,147.52 | |
| 3,207.78 | 2 c | 31,165.23 | | 3,317.01 | 1 | 30,138.99 | |

TABLE 1.—*The arc spectrum of rhenium (Re I)*—Continued

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 3,317.75 | 1 E | 30,132.27 | | 3,405.89 | 15 c | 29,352.51 | 6-72 |
| 3,318.67 | 4 | 30,123.91 | | 3,406.38 | 1 | 29,348.29 | |
| 3,320.66 | 1 | 30,105.86 | | 3,408.15 | 1 | 29,333.05 | |
| 3,321.46 | 2 | 30,098.61 | | 3,408.68 | 4 c | 29,328.48 | |
| 3,322.21 | 2 | 30,091.82 | 6- 77 | 3,409.83 | 5 | 29,318.59 | 15- 90 |
| 3,322.49 | 40 cw | 30,089.28 | 3- 64 | 3,412.69 | 1 | 29,294.02 | |
| 3,324.93 | 3 | 30,067.20 | 11- 88 | 3,413.74 | 3 | 29,285.01 | |
| 3,326.88 | 1 c? | 30,049.57 | | 3,414.36 | 1 | 29,279.70 | |
| 3,327.20 | 2 | 30,046.69 | | 3,416.02 | 1 | 29,265.47 | |
| 3,327.71 | 2 | 30,042.08 | | 3,417.78 | 6 c | 29,250.40 | 9- 77 |
| 3,328.17 | 1 | 30,037.93 | | 3,419.27 | 1 | 29,237.66 | 2- 57 |
| 3,331.52 | 6 | 30,007.73 | 6- 76 | 3,419.41 | 20 | 29,236.46 | 6- 71 |
| 3,335.37 | 7 cw | 29,973.09 | 2- 63 | 3,420.76 | 4 c | 29,224.92 | 2- 55 |
| 3,337.28 | 1 | 29,955.94 | | 3,421.58 | 2 | 29,217.92 | |
| 3,338.18 | 60 | 29,947.86 | 18-107 | 3,424.61 | 200 cw v | 29,192.06 | 3- 58 |
| 3,339.69 | 4 c | 29,934.32 | | 3,426.19 | 7 | 29,178.60 | 15- 89 |
| 3,340.29 | 1 | 29,928.94 | | 3,427.61 | 7 cw | 29,166.51 | 9- 76 |
| 3,341.01 | 1 | 29,922.50 | | 3,428.51 | 1 | 29,158.86 | 19-109 |
| 3,342.25 | 50 | 29,911.39 | 18-106 | 3,428.84 | 1 | 29,156.05 | |
| 3,344.33 | 30 | 29,892.79 | 18-105 | 3,431.83 | 1 | 29,130.65 | 10- 79 |
| 3,346.19 | 20 | 29,876.18 | 5- 73 | 3,432.68 | 1 | 29,123.44 | |
| 3,346.60 | 1 | 29,872.52 | | 3,433.72 | 7 | 29,114.62 | |
| 3,347.58 | 2 c | 29,863.77 | | 3,433.82 | 1 E | 29,113.77 | |
| 3,349.90 | 2 | 29,843.09 | 9- 79 | 3,437 72 | 8 | 29,080.74 | 8- 73 |
| 3,351.17 | 1 | 29,831.78 | | 3,440.85 | 1 | 29,054.29 | |
| 3,351.94 | 1 | 29,824.93 | | 3,441.25 | 3 c | 29,050.91 | |
| 3,353.21 | 4 c | 29,813.63 | 12- 86 | 3,442.97 | 2 | 29,036.40 | 11- 82 |
| 3,355.29 | 5 c | 29,795.15 | | 3,444.99 | 1 h | 29,019.36 | 7- 71 |
| 3,355.63 | 2 | 29,792.13 | | 3,446.57 | 2 c | 29,006.07 | |
| 3,355.90 | 2 | 29,789.74 | | 3,449.38 | 10 d, c? | 28,982.44 | |
| 3,356.34 | 4 | 29,785.83 | | 3,450.09 | 1 h | 28,976.48 | |
| 3,356.46 | 3 | 29,784.76 | 12- 85 | 3,450.94 | 1 h | 28,969.34 | |
| 3,356.81 | 1 | 29,781.66 | | 3,451.88 | 600 cWl | 28,961.45 | 1- 23 |
| 3,358.03 | 5 | 29,770.84 | | 3,453.29 | 3 | 28,949.63 | |
| 3,358.57 | 2 | 29,766.05 | 14- 91 | 3,453.50 | 5 | 28,947.87 | 8- 72 |
| 3,359.21 | 4 | 29,760.38 | 20-115 | 3,458.90 | 2 | 28,902.68 | 14- 86 |
| 3,359.80 | 2 | 29,755.16 | 13- 88 | 3,460.47 | 1,000 cWl | 28,889.57 | 1- 22 |
| 3,361.14 | 4 | 29,743.30 | 5- 72 | 3,464.72 | 800 cWl | 28,854.13 | 1- 21 |
| 3,361.84 | 1 | 29,737.10 | | 3,465.99 | 2 | 28,843.56 | 13- 92 |
| 3,362.75 | 6 | 29,729.06 | 2- 61 | 3,467.96 | 10 c | 28,827.17 | 18-102 |
| 3,363.03 | 2 | 29,726.58 | | 3,468.64 | 1 | 28,821.52 | |
| 3,365.74 | 3 | 29,702.64 | | 3,470.85 | 2 h | 28,803.17 | |
| 3,365.82 | 3 | 29,701.94 | | 3,472.00 | 2 h c? | 28,793.63 | |
| 3,366.17 | 2 cw | 29,698.85 | 3- 62 | 3,472.72 | 3 | 28,787.66 | 8- 70 |
| 3,366.89 | 1 | 29,692.50 | 10- 83 | 3,472.87 | 1 | 28,786.42 | 8- 69 |
| 3,367.50 | 3 | 29,687.12 | 8- 77 | 3,473.47 | 2 | 28,781.44 | 15- 85 |
| 3,367.68 | 2 | 29,685.54 | | 3,474.20 | 2 h c? | 28,775.40 | 11- 81 |
| 3,368.61 | 1 | 29,677.34 | | 3,475.18 | 2 d | 28,767.28 | |
| 3,370.89 | 1 | 29,657.27 | | 3,476.02 | 1 | 28,760.33 | |
| 3,377.74 | 4 | 29,597.12 | | 3,476.44 | 5 | 28,756.86 | |
| 3,379.07 | 3 cwE | 29,585.48 | | 3,477.14 | 2 | 28,751.07 | |
| 3,379.71 | 6 c | 29,579.87 | 2- 60 | 3,478.57 | 2 h c? | 28,739.25 | 3- 54 |
| 3,385.76 | 2 | 29,527.02 | | 3,480.39 | 7 | 28,724.22 | 13- 82 |
| 3,389.42 | 5 | 29,495.14 | | 3,480.86 | 8 | 28,720.34 | 8- 68 |
| 3,389.77 | 2 | 29,492.09 | | 3,482.24 | 4 c | 28,708.96 | |
| 3,390.26 | 4 cw | 29,487.83 | | 3,484.37 | 1 | 28,691.41 | |
| 3,391.22 | 1 | 29,479.48 | | 3,484.72 | 1 | 28,688.53 | |
| 3,392.37 | 1 | 29,469.49 | | 3,487.52 | 1 c? | 28,665.50 | |
| 3,394.13 | 2 | 49,454.21 | | 3,488.85 | 1 c? | 28,654.57 | |
| 3,397.20 | 2 | 29,427.59 | | 3,490.86 | 3 | 28,638.07 | |
| 3,397.69 | 1 | 29,423.34 | | 3,491.43 | 1 | 28,633.40 | |
| 3,398.80 | 1 | 29,413.74 | | 3,494.73 | 2 | 28,606.36 | 13- 84 |
| 3,399.29 | 60 cw | 29,409.50 | 3- 60 | 3,495.90 | 3 cWl | 28,596.78 | |
| 3,401.18 | 2 c? | 29,393.16 | | 3,499.52 | 1 | 28,567.20 | |
| 3,404.72 | 10 | 29,362.60 | 2- 58 | 3,502.74 | 1 | 28,540.94 | |

TABLE 1.—*The arc spectrum of rhenium (Re I)*—Continued

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 3,503.06 | 10 | 28,538.34 | 10- 77 | 3,617.87 | 4 cw | 27,632.72 | |
| 3,503.73 | 2 c? | 28,532.88 | | 3,621.46 | 4 c | 27,605.33 | 13- 78 |
| 3,506.39 | 2 | 28,511.23 | 9- 72 | 3,622.21 | 2 c | 27,599.61 | |
| 3,510.89 | 2 | 28,474.69 | | 3,625.90 | 3 | 27,571.53 | 10- 69 |
| 3,512.28 | 6 cWl | 28,463.42 | 13- 81 | 3,629.20 | 2 | 27,546.46 | |
| 3,515.02 | 1 | 28,441.24 | | 3,634.24 | 1 | 27,508.26 | |
| 3,515.75 | 1 | 28,435.33 | | 3,636.78 | 1 | 27,489.05 | |
| 3,516.16 | 1 c? | 28,432.01 | | 3,637.06 | 4 | 27,486.93 | 5- 61 |
| 3,516.65 | 8 c? | 28,428.06 | | 3,637.22 | 1 | 27,485.72 | |
| 3,517.33 | 10 c | 28,422.56 | | 3,637.84 | 15 | 27,481.04 | 2- 47 |
| 3,520.72 | 3 cWl | 28,395.19 | 9- 71 | 3,639.14 | 3 h c? | 27,471.22 | |
| 3,521.74 | 1 | 28,386.97 | | 3,641.48 | 1 | 27,453.57 | |
| 3,522.17 | 1 | 28,383.50 | | 3,642.98 | 2 | 27,442.26 | 3- 48 |
| 3,522.32 | 1 c? | 28,382.29 | | 3,643.73 | 1 | 27,436.61 | |
| 3,526.74 | 2 | 28,346.72 | | 3,645.59 | 2 c? | 27,422.62 | |
| 3,529.21 | 3 | 28,326.89 | | 3,646.65 | 2 c? | 27,414.65 | |
| 3,529.79 | 2 c? | 28,322.23 | | 3,648.25 | 2 c? | 27,402.62 | |
| 3,530.90 | 1 c? | 28,313.33 | | 3,649.49 | 1 c? | 27,393.31 | |
| 3,534.25 | 1 | 28,286.49 | | 3,651.66 | 5 cw | 27,377.03 | |
| 3,534.82 | 4 | 28,281.93 | 13- 79 | 3,651.97 | 20 | 27,374.71 | 12- 73 |
| 3,536.16 | 1 | 28,271.21 | | 3,653.18 | 1 c? | 27,365.64 | |
| 3,537.47 | 15 c | 28,260.74 | 2- 52 | 3,653.62 | 2 | 27,362.35 | 20-112 |
| 3,539.33 | 4 | 28,245.89 | | 3,654.36 | 1 | 27,356.81 | 20-111 |
| 3,539.94 | 2 | 28,241.03 | | 3,654.93 | 1 | 27,352.54 | |
| 3,541.32 | 1 | 28,230.02 | | 3,658.74 | 1 | 27,324.06 | |
| 3,543.68 | 1 | 28,211.22 | | 3,660.52 | 2 c | 27,310.77 | |
| 3,544.35 | 1 | 28,205.89 | | 3,662.13 | 2 | 27,298.77 | |
| 3,548.11 | 1 | 28,176.00 | | 3,663.03 | 1 | 27,292.06 | |
| 3,549.32 | 1 | 28,166.39 | | 3,669.43 | 2 | 27,244.46 | |
| 3,549.89 | 5 | 28,161.87 | 3- 53 | 3,669.78 | 5 | 27,241.86 | 12- 72 |
| 3,551.30 | 6 cw | 28,150.69 | | 3,670.00 | 2 c | 27,240.23 | 3- 46 |
| 3,551.59 | 2 d? | 28,148.39 | | 3,670.37 | 3 c | 27,237.48 | |
| 3,553.65 | 4 c | 28,132.07 | 15- 83 | 3,670.53 | 10 | 27,236.29 | 6- 62 |
| 3,558.95 | 5 c | 28,090.18 | 3- 52 | 3,672.40 | 3 | 27,222.42 | 8- 64 |
| 3,559.41 | 1 | 28,086.55 | 2- 51 | 3,674.17 | 1 | 27,209.31 | |
| 3,561.14 | 1 | 28,072.91 | | 3,676.00 | 2 | 27,195.77 | |
| 3,562.46 | 2 | 28,062.50 | | 3,676.57 | 1 | 27,191.55 | |
| 3,564.73 | 3 | 28,044.64 | | 3,678.39 | 2 | 27,178.10 | |
| 3,565.20 | 1 | 28,040.94 | | 3,680.21 | 2 | 27,164.66 | |
| 3,566.86 | 1 h | 28,027.89 | | 3,681.29 | 2 | 27,156.69 | |
| 3,568.24 | 4 cw | 28,017.05 | | 3,686.45 | 1 | 27,118.67 | |
| 3,570.25 | 5 | 28,001.28 | | 3,688.65 | 1 | 27,102.50 | |
| 3,571.70 | 1 | 27,989.91 | | 3,688.90 | 1 | 27,100.67 | |
| 3,572.81 | 2 | 27,981.21 | 12- 77 | 3,689.52 | 30 cW v? | 27,096.11 | 6- 61 |
| 3,577.34 | 2 | 27,945.78 | | 3,690.38 | 2 | 27,089.79 | |
| 3,579.13 | 10 | 27,931.81 | 10- 73 | 3,691.39 | 4 | 27,082.38 | |
| 3,580.14 | 20 cw l, E | 27,923.93 | | 3,691.48 | 40 c | 27,081.72 | 12- 70 |
| 3,580.97 | 20 c | 27,917.45 | 11- 76 | 3,692.12 | 1 | 27,077.03 | |
| 3,583.03 | 40 c | 27,901.40 | 3- 50 | 3,697.70 | 4 cw | 27,036.17 | |
| 3,585.03 | 2 c | 27,885.84 | | 3,700.36 | 3 cw | 27,016.74 | |
| 3,585.33 | 1 | 27,883.51 | | 3,701.17 | 1 ? | 27,010.82 | |
| 3,590.88 | 2 | 27,840.41 | | 3,702.10 | 1 | 27,004.04 | |
| 3,593.39 | 3 c | 27,820.96 | | 3,703.24 | 20 | 26,995.73 | 5- 57 |
| 3,595.16 | 3 | 27,807.27 | | 3,704.46 | 3 | 26,986.84 | |
| 3,596.23 | 2 | 27,798.99 | 10- 72 | 3,704.85 | 3 c | 26,984.00 | 5- 56 |
| 3,596.38 | 4 | 27,797.84 | 3- 49 | 3,705.01 | 2 | 26,982.83 | 5- 55 |
| 3,596.76 | 3 | 27,779.45 | | 3,705.68 | 2 c | 26,977.95 | 15- 77 |
| 3,604.40 | 3 c | 27,735.98 | | 3,708.77 | 1 | 26,955.47 | |
| 3,606.55 | 1 | 27,719.45 | | 3,709.93 | 10 | 26,947.05 | 6- 60 |
| 3,607.22 | 2 | 27,714.30 | | 3,711.51 | 2 c | 26,935.56 | 8- 63 |
| 3,608.68 | 1 c | 27,703.09 | | 3,712.93 | 1 | 26,925.28 | |
| 3,610.49 | 6 cw | 27,689.20 | | 3,713.16 | 2 c | 26,923.61 | |
| 3,615.36 | 1 | 27,651.91 | | 3,715.02 | 2 | 26,910.13 | |
| 3,617.08 | 20 c | 27,638.76 | 10- 70 | 3,717.29 | 25 cW v | 26,893.70 | 15- 76 |
| 3,617.24 | 5 | 27,637.53 | 10- 69 | 3,725.76 | 100 | 26,832.56 | 20-108 |

TABLE 1.—*The arc spectrum of rhenium* ($Re_I$)—Continued

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 3,726.49 | 2 | 26,827.30 | | 3,869.94 | 15 c | 25,832.90 | 11- 65 |
| 3,726.72 | 3 d | 26,825.65 | | 3,875.26 | 15 c | 25,797.44 | 2- 38 |
| 3,727.50 | 2 | 26,820.03 | | 3,876.88 | 20 cw v | 25,786.66 | 10- 63 |
| 3,731.87 | 4 | 26,788.63 | 13- 69 | 3,878.86 | 2 | 25,773.49 | |
| 3,732.28 | 6 | 26,785.68 | 9- 64 | 3,881.90 | 4 | 25,753.31 | 17- 78 |
| 3,735.00 | 10 cW v | 26,766.18 | 3- 44 | 3,887.49 | 3 | 25,716.28 | |
| 3,735.33 | 50 | 26,763.81 | 20-107 | 3,887.96 | 3 | 25,713.17 | |
| 3,736.85 | 2 c | 26,752.93 | | 3,889.96 | 3 | 25,699.95 | |
| 3,739.59 | 1 | 26,733.32 | | 3,891.39 | 2 | 25,690.50 | |
| 3,740.10 | 40 c | 26,729.68 | {6- 58<br>{7- 60 | 3,893.45 | 1 c? | 25,676.91 | |
| | | | | 3,893.89 | 1 | 25,674.01 | |
| 3,740.41 | 5 | 26,727.47 | 20-106 | 3,895.42 | 1 | 25,663.93 | |
| 3,742.28 | 3 E | 26,714.11 | | 3,896.11 | 4 c | 25,659.38 | |
| 3,745.45 | 20 c | 26,691.50 | 8- 61 | 3,900.89 | 4 | 25,627.95 | 6- 52 |
| 3,746.94 | 2 | 26,680.89 | | 3,901.08 | 2 | 25,626.69 | 3- 38 |
| 3,749.02 | 1 | 26,666.08 | | | | | |
| | | | | 3,902.58 | 1 | 25,616.84 | |
| 3,750.67 | 1 | 26,654.36 | | 3,902.82 | 1 | 25,615.27 | |
| 3,752.78 | 1 ? | 26,639.37 | | 3,905.12 | 2 | 25,600.18 | |
| 3,755.63 | 4 | 26,619.15 | | 3,907.19 | 1 | 25,586.62 | |
| 3,757.63 | 4 cw v | 26,604.98 | 6- 57 | 3,908.21 | 5 | 25,579.94 | |
| 3,761.03 | 1 | 26,580.93 | | | | | |
| 3,763.49 | 5 cw l | 26,563.56 | 7- 59 | 3,910.21 | 1 | 25,566.86 | |
| 3,766.49 | 3 | 542.40 | 8- 60 | 3,911.76 | 1 | 25,556.73 | |
| 3,768.25 | 1 | 26,530.01 | | 3,913.92 | 5 | 25,542.62 | 10- 61 |
| 3,769.30 | 1 | 26,522.62 | | 3,915.22 | 1 | 25,534.14 | |
| 3,770.74 | 1 | 26,512.49 | 7- 58 | 3,917.27 | 25 cw | 25,520.78 | 13- 65 |
| 3,775.46 | 1 | 26,479.34 | | 3,919.10 | 2 c | 25,508.86 | |
| 3,777.66 | 7 | 26,463.92 | 14- 73 | 3,920.86 | 5 cW v | 25,497.42 | |
| 3,780.36 | 2 | 26,445.02 | | 3,921.78 | 2 | 25,491.43 | |
| 3,784.18 | 2 | 26,418.33 | | 3,922.27 | 2 | 25,488.25 | |
| 3,787.21 | 2 | 26,397.19 | | 3,923.59 | 1 cw ? | 25,479.67 | 2- 37 |
| 3,787.52 | 30 c | 26,395.03 | 9- 62 | 3,924.09 | 2 c | 25,476.43 | |
| 3,788.10 | 1 h c? | 26,390.99 | | 3,924.65 | 1 h | 25,472.79 | |
| 3,795.80 | 4 cW l | 26,337.46 | | 3,926.53 | 1 | 25,460.60 | |
| 3,796.60 | 12 cw v | 26,331.91 | 2- 41 | 3,926.84 | 1 | 25,458.59 | |
| 3,797.59 | 7 | 26,325.04 | 8- 58 | 3,927.60 | 10 cW v | 25,453.66 | 6- 51 |
| 3,800.94 | 1 cw? | 26,301.84 | | 3,928.71 | 2 | 25,446.47 | 4- 39 |
| 3,805.41 | 1 he? | 26,270.95 | | 3,929.20 | 1 | 25,443.30 | |
| 3,807.75 | 5 | 26,254.80 | 9- 61 | 3,929.85 | 25 | 25,439.09 | 6- 50 |
| 3,808.20 | 2 | 26,251.70 | | 3,930.52 | 1 h | 25,434.75 | |
| 3,810.10 | 2 | 26,238.61 | 15- 72 | 3,931.20 | 3 | 25,430.35 | 19- 92 |
| 3,812.26 | 2 | 26,223.74 | | 3,934.23 | 1 | 25,410.77 | 7- 52 |
| 3,812.82 | 1 | 26,219.89 | | 3,936.91 | 10 c | 25,393.47 | 10- 60 |
| 3,815.66 | 6 c | 26,200.38 | 8- 57 | 3,941.52 | 3 d, c? | 25,363.77 | |
| 3,817.55 | 5 cW l | 26,187.41 | 8- 55 | 3,942.56 | 2 | 25,357.08 | |
| 3,823.76 | 3 cw | 26,144.88 | | 3,944.35 | 2 | 25,345.57 | |
| 3,827.03 | 4 cW l | 26,122.54 | 15- 71 | 3,944.73 | 6 c | 25,343.13 | |
| 3,827.63 | 2 | 26,118.44 | | 3,945.91 | 10 c | 25,335.55 | 6- 49 |
| 3,828.32 | 6 | 26,113.74 | 2- 39 | 3,950.60 | 4 d, c? | 25,305.48 | |
| 3,829.81 | 4 c | 26,103.58 | 14- 68 | 3,953.24 | 1 | 25,288.58 | |
| 3,832.39 | 2 c | 26,086.00 | | 3,954.43 | 3 c? | 25,280.97 | |
| 3,833.70 | 10 | 26,077.09 | 15- 69 | 3,954.97 | 5 | 25,277.51 | |
| 3,834.23 | 15 | 26,073.49 | 10- 64 | 3,957.37 | 2 | 25,262.18 | |
| 3,836.30 | 6 | 26,059.42 | 7- 54 | 3,958.36 | 2 | 25,255.87 | |
| 3,841.49 | 2 | 26,024.21 | | 3,958.57 | 1 | 25,254.53 | |
| 3,843.43 | 15 cw v | 26,011.07 | 3- 40 | 3,960.57 | 2 | 25,241.77 | |
| 3,846.86 | 1 | 25,987.88 | | 3,961.04 | 15 | 25,238.78 | 5- 47 |
| 3,848.96 | 1 | 25,973.71 | | 3,962.49 | 40 cW v | 25,229.54 | 12- 63 |
| 3,851.99 | 3 | 25,953.28 | | 3,963.27 | 4 | 25,224.58 | 13- 64 |
| 3,852.69 | 1 | 25,948.56 | | 3,963.70 | 2 | 25,221.84 | 7- 50 |
| 3,855.93 | 4 c | 25,926.76 | | 3,964.27 | 1 | 25,218.22 | |
| 3,860.85 | 1 | 25,893.72 | 19- 93 | 3,964.81 | 3 | 25,214.78 | |
| 3,862.09 | 1 | 25,885.40 | | 3,967.41 | 5 cw | 25,198.26 | |
| 3,863.15 | 1 | 25,878.30 | | 3,967.70 | 1 | 25,196.42 | |
| 3,863.77 | 2 | 25,874.15 | 16- 72 | 3,975.40 | 1 | 25,147.61 | |
| 3,864.76 | 1 | 25,867.52 | | 3,975.68 | 3 | 25,145.97 | 11- 62 |

TABLE 1.—*The arc spectrum of rhenium* ($Re_I$)—Continued

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 3,976.77 | 1 h | 25,138.95 | | 4,096.45 | 1 | 24,404.52 | |
| 3,978.62 | 4 c | 25,127.26 | | 4,099.30 | 1? | 24,387.55 | |
| 3,982.28 | 1 h | 25,104.17 | 17–75 | 4,102.16 | 3 h | 24,370.55 | |
| 3,983.43 | 1 h c? | 25,096.92 | | 4,103.78 | 1 | 24,360.93 | |
| 3,983.92 | 3 c | 25,093.83 | | 4,104.42 | 12 | 24,357.13 | |
| 3,984.25 | 4 c, E | 25,091.76 | | 4,106.44 | 3 c | 24,345.15 | |
| 3,987.08 | 2 | 25,073.95 | | 4,106.83 | 2 | 24,342.84 | |
| 3,987.91 | 1 | 25,068.73 | | 4,107.44 | 1 | 24,339.22 | |
| 3,990.67 | 2 | 25,051.39 | 10–57 | 4,107.95 | 1 | 24,336.20 | |
| 3,991.05 | 4 cw | 25,049.00 | 8–51 | 4,108.61 | 3 | 24,332.29 | |
| 3,991.58 | 2 c | 25,045.68 | | 4,110.90 | 30 cwv | 24,318.74 | 14–62 |
| 3,992.73 | 3 cw | 25,038.47 | 10–55 | 4,111.58 | 2 d v | 24,314.71 | |
| 3,994.15 | 1 hc? | 25,029.56 | | 4,112.26 | 2 | 24,310.69 | |
| 3,995.68 | 3 c | 25,019.98 | | 4,113.41 | 8 | 24,303.90 | 6–44 |
| 3,996.92 | 1 c? | 25,012.22 | | 4,114.68 | 1 | 24,296.40 | |
| 4,000.13 | 1 h | 24,992.15 | | 4,121.60 | 25 | 24,255.60 | 18–78 |
| 4,001.18 | 1 | 24,985.59 | 12–61 | 4,122.75 | 2 | 24,248.84 | |
| 4,004.94 | 5 | 24,962.13 | | 4,123.51 | 1 | 24,244.37 | |
| 4,010.31 | 1 | 24,928.71 | | 4,123.82 | 1 | 24,242.55 | |
| 4,011.52 | 6 | 24,921.19 | | 4,124.78 | 3 hc? | 24,236.90 | |
| 4,012.26 | 4 | 24,916.59 | | 4,128.09 | 2 d? | 24,217.47 | |
| 4,014.88 | 2 | 24,900.33 | | 4,130.46 | 2 | 24,203.57 | |
| 4,018.41 | 4 c | 24,878.46 | | 4,132.30 | 6 | 24,192.80 | 5–42 |
| 4,019.13 | 2 | 24,874.00 | 19–90 | 4,133.42 | 80 cW, d | 24,186.24 | 11–54 |
| 4,022.95 | 8 | 24,850.38 | 17–74 | 4,136.45 | 100 | 24,168.52 | 3–36 |
| 4,023.33 | 10 cW v | 24,848.04 | 6–47 | | | | |
| 4,025.07 | 1 | 24,837.29 | | 4,137.59 | 5 | 24,161.86 | 19–84 |
| 4,025.62 | 2 | 24,833.90 | 13–62 | 4,138.52 | 1 | 24,156.44 | |
| 4,026.71 | 1 | 24,827.18 | | 4,142.44 | 1 h | 24,133.58 | |
| 4,027.13 | 1 | 24,824.59 | | 4,142.77 | 1 | 24,131.66 | |
| 4,028.55 | 4 c | 24,815.83 | | 4,144.36 | 60 | 24,122.40 | 15–62 |
| 4,029.62 | 15 cW l | 24,809.25 | 5–45? 15–65 | 4,146.24 | 3 | 24,111.46 | |
| 4,031.31 | 1 c? | 24,798.85 | | 4,148.29 | 2 | 24,099.55 | |
| 4,031.62 | 1 | 24,796.94 | | 4,149.98 | 20 c | 24,089.73 | 5–41 |
| 4,032.15 | 2 | 24,793.68 | | 4,150.54 | 2 | 24,086.48 | |
| 4,033.31 | 30 cw l | 24,786.55 | 9–52 | 4,150.80 | 1 | 24,084.97 | |
| 4,033.62 | 2 c | 24,784.65 | | 4,151.06 | 1 | 24,083.46 | |
| 4,037.51 | 6 | 24,760.77 | | 4,152.30 | 3 | 24,076.27 | |
| 4,039.51 | 1 | 24,748.51 | | 4,152.64 | 8 c | 24,074.30 | 10–52 |
| 4,040.19 | 2 | 24,744.35 | | 4,157.23 | 1 | 24,047.72 | |
| 4,041.31 | 1 | 24,737.49 | | 4,159.92 | 4 | 24,032.17 | |
| 4,045.25 | 1 | 24,713.39 | | 4,160.77 | 2 | 24,027.26 | |
| 4,048.99 | 10 c | 24,690.57 | 11–59 | 4,161.77 | 1 | 24,021.49 | |
| 4,050.93 | 1 | 24,678.74 | | 4,164.09 | 1 | 24,008.11 | |
| 4,061.66 | 1 | 24,613.55 | | 4,165.32 | 1 | 24,001.02 | |
| 4,061.86 | 3 | 24,612.34 | 9–51 | 4,165.98 | 1 | 23,997.21 | |
| 4,064.31 | 2 | 24,597.50 | 9–50 | 4,166.41 | 2 | 23,994.74 | |
| 4,064.92 | 1 c? | 24,593.81 | | 4,168.58 | 3 | 23,982.25 | 15–61 |
| 4,066.96 | 1 | 24,581.47 | | 4,170.40 | 15 | 23,971.78 | |
| 4,067.24 | 1 | 24,579.78 | | 4,173.69 | 1 | 23,952.88 | |
| 4,069.15 | 3 c, E | 24,568.25 | | 4,173.99 | 3 | 23,951.16 | |
| 4,073.05 | 1 | 24,544.72 | 13–60 | 4,175.19 | 3 | 23,944.28 | |
| 4,073.22? | 8 | 24,543.70 | | 4,176.54 | 3 c | 23,936.54 | 9–46 |
| 4,078.12 | 2 | 24,514.21 | | 4,176.88 | 2 | 23,934.59 | |
| 4,079.37 | 3 | 24,506.69 | | 4,178.61 | 2 | 23,924.68 | |
| 4,081.43 | 12 | 24,494.33 | 12–57 | 4,178.85 | 1 | 23,923.31 | |
| 4,083.37 | 4 | 24,482.69 | 12–56 | 4,179.74 | 1 | 23,918.22 | |
| 4,083.60 | 4 | 24,481.31 | 12–55 | 4,182.22 | 1 | 23,904.03 | |
| 4,088.03 | 2 c | 24,454.78 | 18–80 | 4,182.98 | 50 cw | 23,899.69 | 8–44? |
| 4,089.00 | 2 | 24,448.98 | | 4,184.50 | 1 | 23,891.01 | |
| 4,089.41 | 1 | 24,446.53 | | 4,185.72 | 1 h | 23,884.04 | |
| 4,089.92 | 5 c v | 24,443.48 | 8–47 | 4,187.91 | 2 | 23,871.55 | 5–39 |
| 4,091.10 | 1 | 24,436.43 | | 4,188.46 | 1 | 23,868.42 | |
| 4,091.96 | 1 E | 24,431.30 | | 4,190.79 | 1 h | 23,855.15 | |
| 4,092.94 | 1 h | 24,425.45 | | 4,191.90 | 2 | 23,848.83 | |
| | | | | 4,194.67 | 12 c | 23,833.08 | 15–60 |

TABLE 1.—*The arc spectrum of rhenium* ($Re\ I$)—Continued

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 4,195.75 | 4 | 23,826.95 | | 4,316.19 | 2 | 23,162.09 | |
| 4,203.32 | 2 c? | 23,784.04 | | 4,317.13 | 2 h | 23,157.05 | |
| 4,204.55 | 8 c | 23,777.08 | | 4,317.63 | 1 | 23,154.10 | |
| 4,215.50 | 2 | 23,715.32 | | 4,317.94 | 1 | 23,152.70 | |
| 4,221.08 | 30 | 23,683.97 | 2- 34 | 4,318.58 | 4 | 23,149.27 | |
| 4,224.17 | 3 | 23,666.65 | 15- 59 | 4,319.54 | 5 | 23,144.13 | 8- 40 |
| 4,227.45 | 200 c | 23,648.28 | 17- 67 | 4,324.35 | 2 | 23,118.38 | |
| 4,228.74 | 1 | 23,641.07 | | 4,328.70 | 2 | 23,095.15 | |
| 4,232.96 | 4 | 23,617.50 | 16- 61 | 4,329.07 | 2 | 23,093.18 | |
| 4,233.28 | 3 | 23,615.72 | 15- 58 | 4,331.37 | 2 | 23,080.91 | |
| 4,234.43 | 2 c? | 23,609.30 | 11- 53 | 4,332.25 | 30 | 23,076.23 | 8- 39 |
| 4,234.98 | 4 c | 23,606.24 | 18- 75 | 4,335.86 | 3 | 23,057.02 | |
| 4,235.40 | 1 ? | 23,603.90 | | 4,339.69 | 4 | 23,036.67 | 13- 50 |
| 4,236.24 | 4 | 23,599.22 | | 4,342.16 | 2 | 23,023.56 | |
| 4,238.02 | 2 | 23,589.31 | | 4,344.66 | 1 c? | 23,010.31 | |
| 4,238.59 | 3 | 23,586.13 | 17- 66 | 4,345.50 | 1 | 23,005.87 | |
| 4,239.97 | 1 | 23,578.45 | | 4,351.72 | 1 | 22,972.98 | |
| 4,241.17 | 6 | 23,571.78 | 14- 56 | 4,352.44 | 2 hc? | 22,969.19 | |
| 4,241.39 | 15 | 23,570.56 | 14- 55 | 4,357.07 | 4 c | 22,944.77 | |
| 4,241.81 | 1 | 23,568.23 | 19- 82 | 4,357.96 | 5 | 22,940.09 | |
| 4,243.90 | 1 | 23,556.62 | | 4,358.69 | 50 | 22,936.25 | 2- 31 |
| 4,244.15 | 5 c | 23,555.23 | 5- 38 | 4,359.31 | 3 | 22,932.99 | 13- 49 |
| 4,246.82 | 7 | 23,540.43 | | 4,360.38 | 4 | 22,927.36 | |
| 4,247.70 | 1 | 23,535.55 | | 4,361.28 | 2 | 22,922.63 | |
| 4,248.36 | 1 | 23,531.89 | | 4,363.36 | 2 c | 22,911.70 | |
| 4,255.12 | 1 | 23,494.51 | | 4,364.13 | 4 | 22,907.66 | |
| 4,255.34 | 1 | 23,493.29 | | 4,364.84 | 3 | 22,903.93 | |
| 4,255.76 | 5 | 23,490.98 | 15- 57 | 4,366.35 | 1 | 22,896.01 | |
| 4,257.61 | 50 c | 23,480.77 | 6- 39 | 4,367.57 | 30 c | 22,889.62 | 11- 48 |
| 4,258.88 | 1 | 23,473.77 | | 4,369.65 | 1 | 22,878.72 | |
| 4,259.89 | 2 | 23,468.20 | 16- 60 | 4,369.76 | 2 | 22,878.14 | 4- 33 |
| 4,260.92 | | 23,462.53 | 9- 44 | 4,373.20 | 2 | 22,860.15 | |
| 4,261.28 | 2 | 23,460.55 | | 4,377.07 | 1 | 22,839.94 | |
| 4,261.44 | 1 c? | 23,459.67 | | 4,377.45 | 2 | 22,837.95 | |
| 4,263.36 | 1 | 23,449.10 | | 4,378.46 | 1 | 22,832.69 | |
| 4,263.78 | 1 | 23,446.79 | | 4,380.89 | 1 h | 22,820.02 | |
| 4,264.26 | 1 | 23,444.15 | | 4,385.44 | 4 | 22,796.35 | |
| 4,264.74 | 1 | 23,441.51 | | 4,386.11 | 1 h | 22,792.86 | |
| 4,267.99 | 1 c? | 23,423.66 | | 4,387.41 | 4 c | 22,786.11 | |
| 4,268.73 | 2 c | 23,419.60 | | 4,387.92 | 1 h | 22,783.46 | |
| 4,269.81 | 2 | 23,413.68 | | 4,388.55 | 1 h | 22,780.19 | |
| 4,274.35 | 3 c | 23,388.81 | | 4,391.35 | 40 c | 22,765.67 | 3- 31 |
| 4,279.19 | 1 | 23,362.35 | | 4,392.15 | 1 | 22,761.52 | |
| 4,280.61 | 2 | 23,354.61 | | 4,392.47 | 30 cw | 22,759.86 | 8- 38 |
| 4,281.70 | 1 h | 23,348.66 | 11- 50 | 4,394.37 | 80 c | 22,750.02 | 10- 44 |
| 4,282.74 | 3 | 23,342.99 | 12- 51 | 4,396.09 | 5 | 22,741.12 | |
| 4,286.09 | 1 | 23,324.75 | | 4,396.79 | 10 | 22,737.50 | 12- 47 |
| 4,286.47 | 2 | 23,322.68 | | 4,397.83 | 1 | 22,732.12 | |
| 4,291.18 | 30 cw | 23,297.08 | 13- 53 | 4,399.82 | 3 c | 22,721.84 | |
| 4,291.64 | 10 | 23,294.58 | { 8- 41<br>10- 47 | 4,402.60 | 15 | 22,707.49 | 9- 40 |
| 4,291.77 | 2 | 23,293.88 | | 4,403.68 | 2 | 22,701.92 | |
| 4,298.21 | 2 h | 23,258.98 | | 4,404.28 | 1 | 22,698.83 | |
| 4,299.92 | 4, E? | 23,249.73 | | 4,406.40 | 30 cw | 22,687.91 | 11- 46 |
| 4,301.07 | 2 | 23,243.51 | | 4,408.67 | 1 h | 22,676.23 | |
| 4,301.79 | 1 | 23,239.62 | | 4,410.39 | 1 | 22,667.39 | |
| 4,302.17 | 2 d? | 23,237.57 | 5- 37 | 4,412.52 | 1 | 22,656.45 | |
| 4,304.41 | 30 | 23,225.48 | 13- 52 | 4,413.50 | 1 | 22,651.41 | |
| 4,304.77 | 1 | 23,223.53 | | 4,415.82 | 30 | 22,639.51 | 9- 39 |
| 4,305.34 | 5 | 23,220.46 | | 4,417.28 | 5 c | 22,632.03 | |
| 4,308.79 | 2 | 23,201.87 | | 4,418.81 | 3 | 22,624.19 | |
| 4,309.48 | 3 | 23,198.15 | | 4,419.86 | 1 | 22,618.82 | |
| 4,310.44 | 1 | 23,192.99 | | 4,423.00 | 2, E? | 22,602.76 | |
| 4,313.33 | 1 | 23,177.45 | | 4,423.81 | 1 | 22,598.62 | |
| 4,314.58 | 5 | 23,170.74 | | 4,425.77 | 2 | 22,588.62 | |
| 4,315.74 | 10 cW | 23,164.51 | 6- 38 | 4,426.47 | 1 h | 22,585.04 | |

TABLE 1.—*The arc spectrum of rhenium* ($Re\ I$)—Continued

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 4, 427. 67 | 1 | 22, 578. 92 | | 4, 559. 25 | 10 | 21, 927. 31 | 10- 39 |
| 4, 427. 95 | 4 c | 22, 577. 50 | 13- 48 | 4, 559. 69 | 15 | 21, 925. 19 | 5- 35 |
| 4, 428. 86 | 1 | 22, 572. 86 | | 4, 562. 30 | 1 | 21, 912. 65 | |
| 4, 432. 83 | 1 | 22, 552. 64 | | 4, 563. 23 | 1 | 21, 908. 18 | |
| 4, 434. 23 | 1 | 22, 545. 52 | | 4, 563. 63 | 3 c? | 21, 906. 26 | |
| 4, 436. 62 | 2 | 22, 533. 38 | 19- 77 | 4, 564. 62 | 2 | 21, 901. 51 | 13- 44 |
| 4, 440. 44 | 15 cw | 22, 513. 99 | 15- 52 | 4, 565. 31 | 10 | 21, 898. 20 | |
| 4, 446. 00 | 1 h | 22, 485. 84 | | 4, 565. 49 | 15 | 21, 897. 34 | 12- 43 |
| 4. 448. 15 | 1 | 22, 474. 97 | | 4, 568. 74 | 1 h | 21, 881. 76 | |
| 4, 448. 26 | 2 | 22, 474. 41 | | 4, 571. 91 | 1 c? | 21, 866. 59 | |
| 4, 453. 88 | 8 | 22, 446. 05 | | 4, 572. 18 | 2 | 21, 865. 30 | |
| 4, 454. 65 | 50 cW | 22, 442. 17 | 8- 37 | 4, 574. 39 | 1 h | 21, 854. 73 | |
| 4, 456. 38 | 2 | 22, 433. 46 | | 4 575. 01 | 2 | 21, 851. 77 | |
| 4, 456. 69 | 3 | 22, 431. 90 | | 4, 575. 99 | 2 hc? | 21, 847. 09 | |
| 4 457. 48 | 2 | 22 427. 93 | | 4, 577. 53 | 2 | 21, 839. 74 | |
| 4, 458. 13 | 1 | 22, 424. 66 | | 4, 578. 24 | 2 | 21, 836. 36 | |
| 4, 459. 39 | 1 | 22, 418. 32 | | 4, 578. 92 | 1 | 21, 833. 11 | |
| 4, 463. 51 | 6 | 22, 397. 63 | | 4, 580. 67 | 30. | 21. 824. 77 | 2- 26 |
| 4, 464. 62 | 2 | 22, 392. 06 | | 4, 586. 06 | 2 c | 21, 799. 12 | |
| 4, 465. 84 | 2 | 22, 385. 94 | | 4, 587. 13 | 4 | 21, 794. 04 | 19- 72 |
| 4, 467. 55 | 6 | 22, 377. 37 | | 4, 588. 95 | 2 | 21, 785. 39 | |
| 4, 467. 93 | 15 c | 22, 375. 47 | 13- 46 | 4, 590. 56 | 1 h | 21, 777. 75 | |
| 4, 473. 24 | 1 | 22, 348. 91 | | 4, 591. 67 | 8 | 21, 772. 49 | |
| 4, 473. 92 | 1 | 22, 345. 51 | | 4, 592. 54 | 3 | 21, 768. 36 | |
| 4, 475. 09 | 25 | 22, 339. 67 | 15- 51 | 4, 595. 25 | 2 | 21, 755. 53 | |
| 4, 477. 64 | 2 | 22, 326. 95 | | 4, 597. 31 | 3 c? | 21, 745. 78 | |
| 4, 477. 99 | 10 c | 22, 325. 20 | 15- 50 | 4, 598. 14 | 3 | 21, 741. 85 | |
| 4, 478. 39 | 25 | 22, 323. 21 | | 4, 599. 76. | 1 | 21, 734. 19 | 15- 47 |
| 4, 481. 45 | 4 | 22, 307. 97 | 12- 45 | 4, 605. 72 | 50 | 21, 706. 07 | 6- 36 |
| 4, 486. 58 | 2 c? | 22, 282. 46 | | 4, 607. 79 | 1 h | 21, 696. 32 | |
| 4, 487. 00 | 2 | 22, 280. 38 | | 4, 608. 80 | 3 | 21, 691. 56 | 12- 42 |
| 4, 494. 10 | 2 | 22, 245. 18 | | 4, 609. 80 | 1 | 21, 686. 86 | |
| 4, 495. 10 | 1 h | 22, 240. 23 | | 4, 613. 06 | 1 | 21, 671. 53 | |
| 4, 496. 44 | 6 | 22, 233. 60 | 9- 38 | 4, 613. 96 | 2 | 21, 667. 31 | |
| 4, 498. 38 | 3 | 22, 224. 01 | | 4, 614. 68 | 12 cw | 21, 663. 93 | 15- 46 |
| 4, 499. 04 | 1 | 22, 220. 75 | | 4, 616. 61 | 8 cw | 21, 654. 87 | |
| 4, 504. 42 | 2 | 22, 194. 21 | 4- 30 | 4, 619. 76 | 1 h | 21, 640. 10 | |
| 4, 507. 03 | 40 | 22, 181. 36 | 21-114 | 4, 621. 39 | 25 | 21, 632. 47 | 19- 69 |
| 4, 507. 99 | 20 | 22, 176. 64 | 21-113 | 4, 623. 34 | 2 | 21, 623. 35 | |
| 4, 513. 31 | 300 c | 22, 150. 50 | 18- 67 | 4, 424. 73 | 1 h | 21, 616. 85 | |
| 4, 514. 27 | 5 | 22, 145. 78 | 10- 41<br>22-114 | 4, 625. 98 | 10 c | 21, 611. 01 | 10- 38 |
| | | | | 4, 628. 75 | 1 | 21, 598. 08 | |
| 4, 515. 13 | 3 | 22, 141. 57 | | 4, 630. 24 | 4 c | 21, 591. 13 | |
| 4, 515. 90 | 1 | 22, 137. 79 | | 4, 630. 83 | 30 c | 21, 588. 37 | 12- 41 |
| 4, 516. 63 | 50 | 22, 134. 21 | 21-111 | 4, 634. 40 | 4 cw | 21, 571. 74 | |
| 4, 518. 57 | 1 | 22, 124. 71 | | | | | |
| 4, 519. 76 | 20 c | 22, 118. 89 | 21-110 | 4, 635. 78 | 2 | 21, 565. 32 | |
| 4, 522. 71 | 100 | 22, 104. 46 | 22-112 | 4, 640. 34 | 1 | 21, 544. 13 | |
| 4, 523. 87 | 30 | 22, 098. 79 | 22-111 | 4, 640. 91 | 1 | 21, 541. 49 | |
| 4, 525. 97 | 30 c | 22, 088. 54 | 18- 66 | 4, 641. 38 | 1 | 21, 539. 31 | |
| 4, 526. 95 | 4 hc? | 22, 083. 76 | | 4, 642. 70 | 2 h | 21, 533. 18 | |
| 4, 528. 95 | 15 | 22, 074. 00 | 23-114 | 4, 644. 95 | 6 c | 21, 522. 75 | |
| 4, 529. 92 | 40 c | 22, 069. 28 | 23-113 | 4, 646. 26 | 1 | 21, 516. 68 | |
| 4, 530. 89 | 10 | 22. 064. 55 | | 4, 647. 47 | 4 c | 21, 511. 08 | |
| 4, 531. 36 | 1 | 22, 062. 26 | | 4, 648. 58 | 3 | 21, 505. 94 | 22-107 |
| 4, 536. 01 | 10 | 22, 039. 65 | | 4, 649. 20 | 1 | 21, 503. 08 | |
| 4, 537. 55 | 2 | 22, 032. 17 | | 4, 649. 73 | 2 | 21, 500. 62 | |
| 4, 539. 10 | 2 cw | 22, 024. 64 | | 4, 650. 08 | 2 | 21, 499. 01 | |
| 4, 541. 81 | 15 | 22, 011. 50 | 23-110 | 4, 650. 83 | 2 | 21, 495. 54 | |
| 4, 545. 16 | 30 | 21, 995. 28 | 10- 40 | 4, 651. 19 | 1 | 21, 493. 88 | |
| 4, 545. 53 | 3 | 21, 993. 49 | | 4, 651. 82 | 2 | 21, 490. 97 | |
| 4, 549. 20 | 2 | 21, 975. 75 | | 4, 652. 32 | 3 c | 21, 488. 66 | 7- 36 |
| 4, 550. 49 | 2 cw, E | 21, 969. 52 | | 4, 652. 81 | 1 h | 21, 486. 39 | 21-105 |
| 4, 551. 49 | 2 | 21, 964. 69 | | 4, 654. 56 | 4 c | 21, 478. 32 | 21-104 |
| 4, 556. 01 | 2 | 21, 942. 90 | | 4, 656. 49 | 5 d | 21, 469. 41 | 22-106 |
| 4, 557. 31 | 2 c | 21, 936. 64 | | 4, 657. 33 | 1 | 21, 465. 54 | |

TABLE 1.—*The arc spectrum of rhenium (Re I)*—Continued

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 4,660.53 | 4 | 21,450.80 | 22-105 | 4,806.03 | 1 h | 20,801.40 | |
| 4,661.48 | 3 | 21,446.43 | | 4,810.10 | 3 | 20,783.80 | |
| 4,662.49 | 10 | 21,441.78 | 5- 34 | 4,811.20 | 3 | 20,779.04 | |
| 4,663.00 | 2 h | 21,439.44 | | 4,813.13 | 2 | 20,770.71 | |
| 4,665.23 | 2 | 21,429.19 | | 4,814.89 | 1 h | 20,763.12 | |
| 4,666.72 | 2 | 21,422.35 | | 4,816.05 | 2 h | 20,758.12 | |
| 4,674.31 | 4 | 21,387.56 | | 4,818.40 | 1 | 20,748.00 | |
| 4,675.39 | 2 | 21,382.62 | | 4,819.25 | 1 h | 20,744.34 | |
| 4,679.48 | 4 | 21,363.94 | | 4,820.59 | 10 cw | 20,738.57 | |
| 4,681.89 | 1 | 21,352.94 | | 4,822.64 | 1 h | 20,729.76 | |
| 4,682.32 | 15 | 21,350.98 | | 4,825.12 | 1 | 20,719.10 | |
| 4,685.18 | 1 h | 21,337.94 | 4- 28 | 4,829.89 | 3 cw | 20,698.64 | |
| 4,687.85 | 5 | 21,325.79 | | 4,831.95 | 1 h | 20,689.82 | |
| 4,688.82 | 1 h | 21,321.38 | | 4,832.90 | 1 | 20,685.75 | |
| 4,689.55 | 2 | 21,318.06 | | 4,833.98 | 2 c | 20,681.12 | |
| 4,691.45 | 2 | 21,309.43 | | 4,834.82 | 4 c | 20,677.53 | 14- 41 |
| 4,692.83 | 1 | 21,303.16 | 5- 33 | 4,838.83 | 1 | 20,660.40 | |
| 4,693.39 | 3 | 21,300.62 | | 4,839.63 | 4 | 20,656.98 | |
| 4,695.01 | 15 cw | 21,293.27 | 10- 37 | 4,843.45 | 1 | 20,640.69 | |
| 4,698.08 | 1 | 21,279.36 | | 4,843.74 | 1 | 20,639.46 | |
| 4,699.69 | 2 | 21,272.07 | | 4,845.68 | 2 | 20,631.19 | |
| 4,700.44 | 10 | 21,268.67 | | 4,846.27 | 2 | 20,628.68 | |
| 4,703.77 | 2 h | 21,253.62 | | 4,848.47 | 10 cw | 20,619.32 | 5- 30 |
| 4,704.12 | 1 | 21,252.03 | | 4,849.23 | 1 | 20,616.09 | |
| 4,705.05 | 20 c | 21,247.83 | | 4,852.58 | 3 c | 20,601.85 | 6- 32 |
| 4,711.24 | 1 | 21,219.92 | | 4,854.08 | 1 | 20,595.49 | |
| 4,712.77 | 6 c | 21,213.03 | | 4,856.72 | 1 | 20,584.30 | |
| 4,725.02 | 3 cw | 21,158.03 | | 4,857.15 | 5 | 20,582.47 | |
| 4,725.94 | 7 | 21,153.91 | | 4,862.54 | 2 | 20,559.66 | |
| 4,727.60 | 25 | 21,146.48 | 13- 40 | 4,863.07 | 2 | 20,557.42 | |
| 4,730.42 | 2 h | 21,133.88 | | 4,864.42 | 1 h | 20,551.71 | |
| 4,731.82 | 2 | 21,127.63 | | 4,866.56 | 1 | 20,542.68 | |
| 4,733.87 | 3 | 21,118.47 | | 4,868.44 | 1 | 20,534.74 | |
| 4,735.34 | 1 | 21,111.92 | | 4,869.70 | 4 cW 1 | 20,529.43 | 16- 43 |
| 4,738.54 | 1 | 21,097.67 | | 4,872.07 | 1 h | 20,519.44 | |
| 4,743.52 | 3 d | 21,075.52 | | 4,872.45 | 1 | 20,517.84 | |
| 4,746.25 | 2 h | 21,063.39 | | 4,874.84 | 3 | 20,507.78 | 8- 33 |
| 4,748.07 | 3 | 21,055.32 | | 4,876.93 | 2 | 20,498.99 | |
| 4,748.39 | 25 c | 21,053.90 | 12- 38 | 4,881.27 | 1 | 20,480.77 | |
| 4,749.03 | 10 | 21,051.06 | 6- 34 | 4,882.95 | 2 | 20,473.72 | |
| 4,751.00 | 3 | 21,042.33 | | 4,889.15 | 2,000 cW 1 | 20,447.76 | 1- 18 |
| 4,751.36 | 4 hc? | 21,040.74 | | 4,892.24 | 1 | 20,434.84 | 15- 40 |
| 4,752.10 | 2 | 21,037.46 | | 4,896.17 | 2 | 20,418.44 | |
| 4,758.86 | 15 | 21,007.58 | 2- 25 | 4,899.42 | 2 | 20,404.90 | |
| 4,759.52 | 1 | 21,004.67 | | 4,899.66 | 2 | 20,403.89 | |
| 4,761.03 | 1 | 20,998.00 | | 4.901.43 | 2 | 20,396.53 | |
| 4,762.29 | 1 | 20,992.45 | 5- 32 | 4,903.73 | 6 cw | 20,386.96 | |
| 4,763.68 | 10 c | 20,986.32 | 14- 43 | 4,904.77 | 1 | 20,382.64 | |
| 4,766.91 | 1 | 20,972.10 | | 4,906.22 | 5 | 20,376.62 | |
| 4,771.80 | 2 | 20,950.61 | | 4,908.56 | 8 | 20,366.90 | 15- 39 |
| 4,777.13 | 1 | 20,927.24 | | 4,909.05 | 2 cw | 20,364.87 | 19- 65 |
| 4,779.00 | 2 | 20,919.05 | | 4,914.36 | 2 | 20,342.86 | |
| 4,781.83 | 1 | 20,906.67 | | 4,915.02 | 25 | 20,340.13 | 4- 25 |
| 4,788.72 | 1 | 20,876.59 | | 4,917.84 | 3 c | 20,328.47 | |
| 4,789.21 | 3 | 20,874.45 | | 4,922.37 | 1 | 20,309.76 | |
| 4,791.42 | 100 c | 20,864.83 | 9- 36 | 4,923.91 | 100 c | 20,303.41 | 6- 31 |
| 4,793.57 | 1 | 20,855.46 | | 4,925.99 | 1 | 20,294.84 | |
| 4,796.91 | 2 | 20,841.95 | | 4,926.91 | 3 | 20,291.05 | |
| 4,799.13 | 4 | 20,831.31 | | 4,928.60 | 1 hc? | 20,284.09 | |
| 4,799.50 | 3 | 20,829.70 | | 4,932.37 | 2 | 20,268.59 | |
| 4,800.78 | 2 cw | 20,824.15 | | 4,933.74 | 7c | 20,262.96 | |
| 4,802.29 | 1 | 20,817.60 | | 4,935.85 | 8 | 20,254.30 | |
| 4,803.34 | 1 | 20,813.05 | | 4,938.64 | 1 h | 20,242.86 | |
| 4,805.19 | 1 | 20,805.04 | | 4,943.73 | 3 c | 20,222.01 | |
| 4,805.54 | 1 | 20,803.52 | | 4,944.88 | 3 | 20,217.31 | |

TABLE 1.—*The arc spectrum of rhenium (Re I)*—Continued

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 4,946.73 | 50 | 20,209.75 | 9–34 | 5,120.32 | 12 | 19,524.60 | |
| 4,949.83 | 5 | 20,197.09 | 8–32 | 5,124.20 | 1 | 19,509.82 | |
| 4,952.26 | 1 | 20,187.18 | | 5,124.59 | 4 | 19,508.34 | |
| 4,955.29 | 2 | 20,174.84 | | 5,126.68 | 10 cW l | 19,500.38 | |
| 4,956.77 | 20 | 20,168.82 | 20–74 | 5,140.03 | 3 | 19,449.74 | |
| 4,960.42 | 1 | 20,153.98 | | 5,141.27 | 2 | 19,445.04 | |
| 4,961.39 | 4 | 20,150.04 | | 5,145.58 | 3 | 19,428.76 | |
| 4,963.07 | 4 c | 20,143.22 | 14–38 | 5,146.90 | 6 cw | 19,423.78 | 12–33 |
| 4,967.82 | 3 | 20,123.96 | | 5,156.25 | 4 c | 19,388.55 | 19–60 |
| 4,969.44 | 4 | 20,117.39 | | 5,161.64 | 6 | 19,368.31 | 16–37 |
| 4,972.84 | 4 | 20,103.64 | | 5,165.19 | 2 | 19,355.00 | |
| 4,974.67 | 2 | 20,096.25 | | 5,167.89 | 1 | 19,344.89 | |
| 4,976.94 | 1 | 20,087.08 | | 5,172.38 | 1 | 19,328.09 | |
| 4,980.68 | 3 c | 20,072.00 | 5–29 | 5,172.72 | 3 c | 19,326.82 | |
| 4,981.54 | 6 | 20,068.53 | 19–64 | 5,178.89 | 15 cw | 19,303.79 | 13–36 |
| 4,984.81 | 2 | 20,055.37 | | 5,181.74 | 5 | 19,293.18 | |
| 4,985.99 | 40 c | 20,050.62 | 15–38 | 5,185.88 | 1 | 19,277.78 | |
| 4,987.52 | 2 | 20,044.47 | | 5,186.14 | 1 | 19,276.81 | 8–29 |
| 4,994.03 | 2 | 20,018.34 | | 5,186.42 | 1 | 19,275.77 | |
| 4,996.42 | 1 | 20,008.76 | | 5,199.88 | 2 h | 19,225.87 | |
| 4,997.74 | 2 | 20,003.48 | | 5,200.84 | 1 h | 19,222.32 | 19–59 |
| 4,999.39 | 2 | 19,996.88 | | 5,214.72 | 2 | 19,171.16 | 19–58 |
| 5,003.59 | 5 | 19,980.09 | | 5,217.44 | 1 | 19,161.17 | |
| 5,008.15 | 3 c | 19,961.90 | | 5,218.22 | 2 | 19,158.30 | |
| 5,010.57 | 2 | 19,952.26 | | 5,221.14 | 2 h | 19,147.59 | |
| 5,011.87 | 1 | 19,947.08 | | 5,222.11 | 2 | 19,144.03 | |
| 5,017.74 | 1 | 19,923.75 | | 5,224.73 | 6+Ag g | 19,134.43 | |
| 5,024.01 | 1 | 19,898.89 | 8–31 | 5,234.31 | 5 c | 19,099.41 | |
| 5,026.44 | 6 | 19,889.26 | | 5,236.65 | 4 c | 19,090.88 | |
| 5,027.93 | 5 | 19,883.37 | | 5,244.32 | 3 | 19,062.96 | |
| 5,029.77 | 1 h | 19,876.10 | | 5,245.50 | 1 h | 19,058.67 | |
| 5,031.56 | 1 | 19,869.03 | | 5,248.85 | 8 | 19,046.51 | 19–57 |
| 5,031.94 | 1 | 19,867.53 | | 5,250.05 | 2 h | 19,042.15 | |
| 5,036.84 | 1 | 19,848.20 | | 5,252.33 | 2 | 19,033.89 | |
| 5,041.39 | 1 h | 19,830.28 | | 5,260.59 | 2 c v? | 19,004.00 | |
| 5,042.63 | 4 cw | 19,825.41 | 14–37 | 5,262.37 | 2 h c? | 18,997.57 | |
| 5,052.21 | 2 h | 19,787.82 | | 5,264.40 | 2 | 18,990.25 | |
| 5,054.36 | 1 | 19,779.40 | | 5,264.40 | 2 | 18,990.25 | |
| 5,054.95 | 1 | 19,777.09 | | 5,265.12 | 2 | 18,987.65 | |
| 5,056.05 | 3 | 19,772.79 | | 5,270.96 | 500 c | 18,966.61 | 20–67 |
| 5,058.55 | 25 | 19,763.02 | 5–28 | 5,275.54 | 1,000 cW l | 18,950.15 | 1–17 |
| 5,060.43 | 3 | 19,755.67 | | 5,278.24 | 30 | 18,940.45 | 12–34 |
| 5,063.74 | 3 | 19,742.76 | | 5,279.07 | 1 | 18,937.47 | |
| 5,065.30 | 2 | 19,736.68 | | 5,284.58 | 2 | 18,917.73 | |
| 5,067.53 | 2 | 19,728.00 | | 5,286.76 | 1 h | 18,909.93 | |
| 5,068.88 | 2 h | 19,722.74 | | 5,287.92 | 3 c | 18,905.78 | |
| 5,072.72 | 1 h | 19,707.81 | | 5,291.37 | 2 cw | 18,893.45 | |
| 5,078.40 | 3 | 19,685.77 | 16–38 | 5,292.27 | 2 | 18,890.24 | |
| 5,081.58 | 1 | 19,673.45 | | 5,296.70 | 1 cw | 18,874.44 | |
| 5,087.64 | 1 | 19,650.02 | | 5,300.76 | 3 c? | 18,859.99 | |
| 5,090.55 | 3 | 19,638.78 | | 5,305.56 | 10 | 18,842.92 | |
| 5,093.18 | 2 | 19,628.64 | | 5,306.72 | 2 | 18,838.80 | |
| 5,094.03 | 2 | 19,625.37 | | 5,309.89 | 1 | 18,827.55 | |
| 5,095.77 | 4 d v | 19,618.67 | | 5,311.53 | 3 c | 18,821.74 | |
| 5,096.48 | 30 c | 19,615.93 | 11–36 | 5,317.28 | 8 c | 18,801.39 | |
| 5,098.75 | 1 | 19,607.20 | | 5,319.24 | 1 | 18,794.46 | |
| 5,100.69 | 1 | 19,599.75 | | 5,321.27 | 10 | 18,787.30 | 8–26 |
| 5,104.63 | 8 cw | 19,584.62 | 5–27 | 5,321.50 | 1 | 18,786.48 | |
| 5,105.14 | 3 | 19,582.66 | 5–26 | 5,325.19 | 1 v n? | 18,773.46 | |
| 5,108.76 | 4 | 19,568.78 | | 5,327.46 | 30 | 18,765.46 | 5–25 |
| | | | | 5,331.88 | 15 c | 18,749.91 | 10–31 |
| 5,112.25 | 6 | 19,555.43 | | 5,332.48 | 1 ? | 18,747.80 | |
| 5,113.24 | 1 | 19,551.64 | | 5,332.76 | 4 | 18,746.81 | |
| 5,115.21 | 1 h c? | 19,544.11 | | 5,333.85 | 8 | 18,742.98 | |
| 5,116.88 | 1 | 19,537.73 | 19–61 | 5,338.62 | 3 | 18,726.24 | |
| 5,117.40 | 1 | 19,535.74 | | 5,339.40 | 3 | 18,723.50 | |

TABLE 1.—*The arc spectrum of rhenium (Re I)*—Continued

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 5,342.35 | 2 | 18,713.16 | | 5,612.27 | 4 c | 17,813.17 | |
| 5,343.72 | 2 c? | 18,708.37 | | 5,619.76 | 2 | 17,789.43 | |
| 5,345.20 | 1 | 18,703.19 | | 5,621.20 | 1 | 17,784.87 | |
| 5,349.23 | 2 | 18,689.10 | | 5,625.45 | 3 c | 17,771.43 | |
| 5,350.43 | 3 cw | 18,684.90 | | 5,635.45 | 1 | 17,739.90 | |
| 5,352.62 | 1 | 18,677.26 | | 5,644.46 | 2 | 17,711.58 | |
| 5,353.30 | 2 | 18,674.89 | | 5,653.02 | 4 | 17,684.76 | |
| 5,353.71 | 1 | 18,673.46 | | 5,658.69 | 2 h | 17,667.04 | |
| 5,356.66 | 1 | 18,663.17 | | 5,662.86 | 2 c | 17,654.03 | |
| 5,366.64 | 1 | 18,628.47 | | 5,664.71 | 2 | 17,648.27 | |
| 5,369.45 | 10 | 18,618.72 | | 5,665.03 | 1 | 17,647.27 | |
| 5,369.80 | 10 | 18,617.50 | 5- 24 | 5,667.88 | 40 | 17,638.40 | 10- 26 |
| 5,374.69 | 3 | 18,600.56 | | 5,671.04 | 2 | 17,628.57 | |
| 5,377.08 | 100 cw l | 18,592.30 | 15- 36 | 5,672.68 | 1 c? | 17,623.47 | |
| 5,378.15 | 3 | 18,588.60 | | 5,680 92 | 2 | 17,597.91 | |
| 5,379.69 | 2 | 18,583.28 | | 5,684.32 | 1 | 17,587.39 | |
| 5,390.20 | 1 ? | 18,547.04 | | 5,689.75 | 3 c | 17,570.60 | 12- 29 |
| 5,396.47 | 4 | 18,525.50 | | 5,706.51 | 2 | 17,519.00 | |
| 5,402.18 | 2 | 18,505.92 | | 5,711.43 | 8 | 17,503.90 | |
| 5,409.50 | 1 | 18,480.87 | | 5,714.03 | 3 | 17,495.94 | |
| 5,410.00 | 1 c? | 18,479.16 | | 5,716.96 | 6 | 17,486.98 | |
| 5,416.26 | 1 | 18,457.81 | | 5,725.64 | 4 | 17,460.46 | |
| 5,417.74 | 2 c | 18,452.77 | | 5,727.89 | 2 | 17,453.60 | |
| 5,420.44 | 1 h? | 18,443.57 | | 5,732.26 | 1 ? | 17,440.30 | |
| 5,421.75 | 2 | 18,439.12 | | 5,733.05 | 3 c ? | 17,437.90 | |
| 5,423.28 | 1 | 18,433.92 | | 5,734.28 | 2 hc | 17,434.16 | 16- 33 |
| 5,423.59 | 3 | 18,432.86 | | 5,734.80 | 1 | 17,432.58 | |
| 5,423.77 | 3 | 18,432.25 | | 5,736.27 | 1 | 17,428.11 | |
| 5,431.87 | 8 | 18,404.76 | | 5,737.35 | 1 hc ? | 17,424.83 | |
| 5,437.01 | 4 | 18,387.36 | | 5,738.08 | 1 c ? | 17,422.61 | |
| 5,437.39 | 1 | 18,386.08 | | 5,739.44 | 3 | 17,418.48 | |
| 5,447.89 | 4 | 18,350.64 | 9- 26 | 5,740.29 | 5 cW l | 17,415.90 | |
| 5,449.65 | 1 | 18,344.72 | | 5,752.92 | 100 cw l | 17,377.67 | 2- 23 |
| 5,456.28 | 1 | 18,322.42 | | 5,763.40 | 1 ? | 17,346.07 | |
| 5,460.62 | 4 | 18,307.86 | | 5,776.81 | 200 cW l | 17,305.80 | 2- 22 |
| 5,480.99 | 2 | 18,239.82 | | 5,778.30 | 2 d v ? | 17,301.34 | |
| 5,495.70 | 1 h? | 18,191.00 | | 5,783.01 | 1 | 17,287.25 | |
| 5,501.91 | 3 | 18,170.47 | | 4,786.21 | 4 c v | 17,277.69 | |
| 5,505.64 | 2 h | 18,158.16 | | 5,791.59 | 7 | 17,261.64 | 12- 28 |
| 5,519.52 | 2 c | 18,112.50 | | 5,796.25 | 1 | 17,247.76 | |
| 5,520.04 | 4 c | 18,110.79 | | 5,806.96 | 5 | 17,215.95 | |
| 5,521.09 | 6 | 18,107.35 | | 5,807.42 | 2 hc | 17,214.59 | |
| 5,521.82 | 1 c? | 18,104.95 | | 5,808.84 | 5 c | 17,210.38 | |
| 5,523.41 | 5 cw | 18,099.74 | | 5,810.66 | 1 h | 17,204.99 | |
| 5,524.22 | 1 d? | 18,097.09 | | 5,810.96 | 1 | 17,204.10 | |
| 5,529.97 | 1 | 18,078.27 | | 5,815.89 | 8 cw | 17,189.52 | 15- 31 |
| 5,532.67 | 25 cw | 18,069.45 | 19- 52 | 5,818.08 | 1 | 17,183.05 | |
| 5,535.93 | 1 h | 18,058.81 | | 5,818.24 | 1 | 17,182.58 | |
| 5,540.13 | 1 h? | 18,045.12 | | 5,834.31 | 500 | 17,135.25 | 3- 22 |
| 5,551.05 | 1 h c? | 18,009.62 | | 5,835.48 | 2 cw | 17,131.82 | |
| 5,557.20 | 3 | 17,989.69 | | 5,851.98 | 10 cW l | 17,083.51 | 12- 27 |
| 5,563.25 | 50 cw | 17,970.13 | 8- 25 | 5,852.73 | 2 | 17,081.32 | 12- 26 |
| 5,564.13 | 4 | 17,967.28 | | 5,866.57 | 4 c ? | 17,041.02 | |
| 5,573.48 | 8 c | 17,937.14 | 15- 34 | 5,868.04 | 3 | 17,036.75 | |
| 5,577.70 | 2 c | 17,923.57 | | 5,870.69 | 1 | 17,029.06 | |
| 5,580.77 | 1 | 17,913.71 | | 5,904.00 | 3 | 16,932.99 | |
| 5,582.90 | 1 | 17,906.88 | | 5,908.02 | 1? | 16,921.47 | |
| 5,584.72 | 8 c | 17,901.04 | 13- 31 | 5,909.98 | 3 | 16,915.85 | |
| 5,592.68 | 1 | 17,875.56 | | 5,911.14 | 3 | 16,912.54 | |
| 5,594.86 | 2 | 17,868.60 | | 5,916.61 | 1 h | 16,896.90 | |
| 5,601.91 | 2 | 17,846.11 | | 5,919.85 | 3 | 16,887.65 | |
| 5,604.16 | 1 | 17,838.95 | | 5,927.38 | 3 cw | 16,866.20 | |
| 5,607.22 | 4 d? l | 17,829.21 | | 5,943.24 | 30 | 16,821.19 | 10- 25 |
| 5,608.79 | 2 | 17,824.23 | | 5,945.48 | 1 h ? | 16,814.85 | |
| 5,610.52 | 2 | 17,818.73 | 10- 28 | 5,947.57 | 1 | 16,808.94 | |

TABLE 1.—*The arc spectrum of rhenium (Re I)*—Continued

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 5, 950. 21 | 4 c | 16, 801. 48 | | 6, 557. 65 | 2 c ? | 15, 245. 16 | |
| 5, 954. 29 | 2 | 16, 789. 97 | | 6, 577. 12 | 15 cW v | 15, 200. 03 | 21- 75 |
| 5, 956. 07 | 1 | 16, 784. 96 | | 6, 592. 54 | 25 cW | 15, 164. 48 | 22- 75 |
| 5, 967. 61 | 2 | 16, 752. 50 | | 6, 605. 19 | 80 d | 15, 135. 44 | 5- 23 |
| 5, 969. 76 | 5 c | 16, 746. 46 | | 6, 611. 65 | 3 c | 15, 120. 65 | |
| 5, 972. 55 | 2 | 16, 738. 64 | | 6, 612. 52 | 4 | 15, 118. 66 | |
| 5, 981. 65 | 2 c | 16, 713. 18 | | 6, 623. 92 | 15 c | 15, 092. 64 | 23- 75 |
| 5, 982. 67 | 3 | 16, 710. 33 | 4- 23 | 6, 637. 23 | 6 cw | 15, 062. 37 | |
| 5, 983. 14 | 2 | 16, 709. 01 | | 6, 652. 36 | 40 c | 15, 028. 12 | 5- 21 |
| 5, 989. 99 | 3 | 16, 689. 90 | | 6, 658. 74 | 1 | 15, 013. 72 | |
| 5, 995. 74 | 4 c | 16, 673. 90 | | 6, 665. 20 | 8 cW l | 14, 998. 96 | |
| 6, 029. 05 | 1 h | 16, 581. 78 | | 6, 683. 30 | 6 c | 14, 958. 55 | |
| 6, 036. 32 | 2 | 16, 561. 81 | | 6, 688. 73 | 2 | 14, 946. 40 | 21- 74 |
| 6, 039. 68 | 3 cw | 16, 552. 60 | | 6, 695. 15 | 2 c ? | 14, 932. 07 | |
| 6, 051. 16 | 2 | 16, 521. 19 | | 6, 711. 29 | 8 c | 14, 896. 16 | 16- 25 |
| 6, 081. 56 | 1 ? | 16, 438. 61 | | 6, 723. 56 | 1 p ? | 14, 868. 98 | |
| 6, 114. 20 | 6 | 16, 350. 85 | 14- 28 | 6, 724. 95 | 2 | 14, 865. 90 | |
| 6, 125. 44 | 2 | 16, 320. 85 | | 6, 751. 22 | 25 | 14, 808. 06 | |
| 6, 132. 97 | 2 c | 16, 300. 81 | | 6, 761. 19 | 5 c | 14, 786. 22 | |
| 6, 145. 80 | 6 cw | 16, 266. 78 | | 6, 799. 57 | 4 cw | 14, 702. 76 | |
| 6, 146. 82 | 8 c | 16, 264. 08 | 12- 25 | 6, 801. 65 | 4 | 14, 698. 26 | |
| 6, 169. 58 | 2 c | 16, 204. 09 | | 6, 805. 36 | 4 c ? | 14, 690. 25 | |
| 6, 176. 56 | 2 cw | 16, 185. 77 | | 6, 811. 37 | 2 | 14, 677. 29 | |
| 6, 181. 68 | 1 | 16, 172. 37 | 14- 27 | 6, 813. 42 | 200 d l | 14, 672. 87 | 6- 22 |
| 6, 187. 90 | 2 | 16, 156. 11 | | 6, 816. 40 | 1 | 14, 666. 46 | |
| 6, 195. 45 | 4 c v ? | 16, 136. 42 | | 6, 829. 96 | 200 d | 14, 637. 34 | 6- 21 |
| 6, 200. 73 | 1 | 16, 122. 68 | | 6, 835. 35 | 2 | 14, 625. 80 | |
| 6, 203. 24 | 4 c ? | 16, 116. 16 | 12- 24 | 6, 844. 06 | 2 | 14, 607. 19 | |
| 6, 217. 98 | 6 | 16, 077. 95 | 15- 26 | 6, 844. 44 | 2 | 14, 606. 38 | |
| 6, 218. 76 | 1 hc ? | 16, 075. 94 | | 6, 874. 38 | 3 | 14, 542. 76 | |
| 6, 229. 44 | 8 cW v | 16, 048. 38 | 21- 80 | 6, 882. 1 | 1 | 14, 526. 4 | |
| 6, 243. 28 | 10 cW v | 16, 012. 80 | 22- 80 | 6, 963. 57 | 1 | 14, 356. 50 | |
| 6, 247. 58 | 1 d | 16, 001. 78 | | 6, 967. 67 | 3 | 14, 348. 05 | |
| 6, 252. 06 | 1 | 15, 990. 31 | 19- 40 | 6, 971. 52 | 100 c | 14, 340. 13 | 8- 23 |
| 6, 253. 02 | 2 | 15, 987. 86 | | 6, 976. 68 | 1 | 14, 329. 52 | |
| 6, 260. 04 | 4 c ? | 15, 969. 93 | | 6, 985. 19 | 10 cW | 14, 312. 06 | |
| 6, 260. 24 | 6 c ? | 15, 969. 42 | | 7, 006. 62 | 60 cW | 14, 268. 29 | 8- 22 |
| 6, 265. 07 | 2 c ? | 15, 957. 11 | | 7, 012. 52 | 2 | 14, 256. 28 | |
| 6, 271. 40 | 4 cw | 15. 941. 00 | 23- 80 | 7, 024. 12 | 80 d | 14, 232. 74 | 8- 21 |
| 6, 278. 77 | 4 | 15, 922. 29 | 19- 39 | 7, 027. 14 | 1 | 14, 226. 63 | |
| 6, 286. 40 | 3 c | 15, 902. 97 | | 6, 028. 50 | 4 c ? | 14, 223. 87 | |
| 6, 290. 10 | 2 c ? | 15, 893. 61 | 16- 28 | 7, 058. 23 | 4 c ? | 14, 163. 96 | |
| 6, 303. 42 | 3 | 15, 860. 03 | | 7, 059. 98 | 2 c ? | 14, 160. 43 | |
| 6, 307. 71 | 100 d | 15, 849. 24 | 21- 78 | 7, 066. 46 | 5 | 14, 147. 46 | 19- 36 |
| 6, 321. 89 | 120 d | 15, 813. 69 | 22- 78 | 7, 108. 8 | 1 c ? | 14, 063. 2 | |
| 6, 350. 75 | 80 d | 15, 741. 83 | 23- 78 | 7, 129. 3 | 5 c | 14, 022. 8 | |
| 6, 362. 66 | 1 c ? | 15, 712. 36 | | 7, 135. 30 | 4 | 14, 010. 97 | |
| 6, 362. 93 | 2 c ? | 15, 711. 69 | | 7, 139. 64 | 1 | 14, 002. 46 | |
| 6, 373. 45 | 3 c ? | 15, 685. 76 | | 7, 172. 21 | 5 | 13, 938. 87 | |
| 6, 374. 79 | 3 cw l | 15, 682. 47 | | 7, 198. 41 | 3 c | 13, 888. 13 | |
| 6, 382. 93 | 4 c ? | 15, 662. 47 | | 7, 228. 03 | 4 | 13, 831. 22 | 9- 22 |
| 6, 405. 78 | 1 h | 15, 606. 60 | | 7, 237. 29 | 1 | 13, 813. 53 | |
| 6, 406. 16 | 3 hc. ? | 15, 605. 67 | 19-38? | 7, 246. 65 | 100 d | 13, 795. 68 | 9- 21 |
| 6, 411. 47 | 5 | 15, 592. 75 | | 7, 263. 87 | 2 | 13, 762. 98 | |
| 6, 449. 28 | 2 c ? | 15, 501. 33 | | 7, 273. 80 | 50 cW l | 13, 744. 19 | 21- 67 |
| 6, 473. 44 | 1 | 15, 443. 48 | | 7, 281. 45 | 1 | 13, 729. 75 | |
| 6, 501. 15 | 2 | 15, 377. 65 | | 7, 292. 68 | 120 cW | 13, 708. 60 | 22- 67 |
| 6, 502. 20 | 2 | 15, 375. 17 | | 7, 307. 50 | 2 | 13, 680. 81 | |
| 6, 510. 74 | 1 | 15, 355. 00 | | 7, 315. 89 | 3 c ? | 13, 665. 12 | |
| 6, 511. 48 | 20 c ? | 15, 353. 26 | 14- 25 | 7, 324. 14 | 2 | 13, 649. 68 | |
| 6, 515. 24 | 5 | 15, 344. 40 | | 7, 329. 2 | 3 | 13, 640. 3 | |
| 6, 529. 21 | 2 | 15, 311. 57 | | 7, 452. 01 | 15 c | 13, 597. 98 | |
| 6, 544. 90 | 3 | 15, 274. 86 | | 7, 360. 09 | 3 | 13, 583. 07 | |
| 6, 545. 73 | 2 | 15, 272. 92 | | 7, 386. 37 | 5 | 13, 534. 73 | |
| 6, 554. 63 | 1 | 15, 252. 19 | | 7, 404. 28 | 1 | 13, 501. 99 | |

TABLE 1.—*The arc spectrum of rhenium* ($Re\ I$)—Continued

| Wave length | Intensity and character | Vacuum wave number | Combination | Wave length | Intensity and character | Vacuum wave number | Combination |
|---|---|---|---|---|---|---|---|
| 7,409.45 | 3 | 13,492.57 | 19– 34 | 7,888.79 | 1 | 12,672.73 | |
| 7,440.69 | 2 | 13,435.92 | | 7,898.39 | 3 | 12,657.33 | |
| 7,447.40 | 2 c? | 13,423.81 | | 7,912.90 | 80 c | 12,634.12 | 12– 23 |
| 7,478.69 | 2 | 13,367.65 | | 7,938.54 | 2 | 12,593.31 | |
| 7,481.16 | 2 | 13,363.24 | | 7,971.05 | 4 | 12,541.95 | |
| 7,488.08 | 3 c? | 13,350.89 | | 7,980.70 | 50 c | 12,526.79 | 12– 21 |
| 7,524.46 | 4 c | 13,286.34 | | 8,052.0 | 1 h | 12,415.9 | |
| 7,526.47 | 1 | 13,282.79 | | 8,055.98 | 1 | 12,409.73 | |
| 7,536.51 | 1 c? | 13,265.09 | | 8,059.98 | 3 | 12,403.57 | |
| 7,545.31 | 1 c? | 13,249.62 | | 8,088.16 | 2 | 12,360.36 | |
| 7,548.70 | 5 | 13,243.67 | | 8,166.51 | 1 | 12,241.77 | |
| 7,567.83 | 2 | 13,210.20 | | 8,185.16 | 3 N? | 12,213.88 | |
| 7,578.70 | 100 cw | 13,191.25 | 10– 23 | 8,293.63 | 3 | 12,054.14 | |
| 7,605.77 | 2 ? | 13,144.30 | | 8,300.95 | 3 | 12,043.51 | |
| 7,611.87 | 20 | 13,133.76 | | 8,312.93 | 1 | 12,026.14 | |
| 7,620.19 | 60 cw | 13,119.42 | 10– 22 | 8,357.52 | 3 | 11,961.99 | |
| 7,640.91 | 200 cW | 13,083.83 | 10– 21 | 8,361.75 | 2 | 11,955.94 | |
| 7,693.66 | 2 | 12,994.15 | | 8,399.56 | 1 | 11,902.12 | |
| 7,705.94 | 3 | 12,973.44 | | | | | |
| 7,733.59 | 3 | 12,927.06 | | 8,417.10 | 60 c | 11,877.32 | 3– 20 |
| | | | | 8,527.68 | 40 c | 11,723.30 | 14– 23 |
| 7,743.12 | 1 | 12,911.14 | | 8,570.74 | 1 | 11,665.40 | |
| 7,769.84 | 3 | 12,866.74 | | 8,644.8 | 5 h c | 11,564.5 | |
| 7,789.94 | 1 | 12,833.54 | | | | | |
| 7,794.73 | 1 | 12,825.65 | | 8,575.5 | 1 h | 11,523.6 | 15– 21 |
| 7,825.84 | 3 | 12,774.67 | | 8,705.1 | 2 h | 11,484.4 | |
| | | | | 8,786.7 | 2 | 11,377.7 | |
| 7,828.11 | 2 | 12,770.96 | | 8,797.6 | 2 | 11,363.6 | |
| 7,844.13 | 2 | 12,744.89 | 19– 31 | | | | |
| 7,869.58 | 5 cw | 12,703.67 | | | | | |
| 7,880.74 | 1 | 12,685.68 | | | | | |
| 7,882.10 | 3 | 12,683.49 | | | | | |

Each rhenium spectrogram had an exposure to the iron arc either juxtaposed or superposed and all wave-length measurements were made relative to the international secondary standards[12] except in the interval 2,500 to 3,370 A where the iron values of Burns corrected[13] to the international scale were used. Each plate was measured in both directions, and every line was observed on at least two different plates so that each of the final mean values presented in Table 1, represents at least 4 and frequently 6, 8, or 10 micrometric readings. The average probable error is of the order of $\pm 0.01$ A except for the red and infra-red lines in which the hyperfine structure is, in general, coarser and less regular so that somewhat larger errors may occur. Complete results are compiled in Table 1 in which the wave lengths appear in column 1, estimated relative intensity and line character in column 2, wave number in vacuo in column 3, and term combinations in the last.

After the wave-length data were compiled they were carefully examined for impurities by comparison with the raies ultimes[14] of the chemical elements and with Kayser's table of principal lines.[15] The purity of the $KReO_4$ was thus seen to be exceedingly high. One line of Li (6,707.85 A) and one of Rb (7,800.30 A) were faintly present, probably as impurities in the potassium. Fe, Cu, Na, Ca, were recognized as impurities in the silver electrodes, but these and the

[12] Trans. Int. Astron. Union, III, p. 86; 1928.
[13] K. Burns, Pub. Allegheny Observatory, 8, No. 1; 1930.
[14] W. F. Meggers, International Critical Tables, V. p. 322.
[15] H. Kayser, Tabelle der Hauptlinien, Julius Springer, Berlin.

silver lines themselves were ignored in measuring the spectrograms. Among the remaining lines, which number more than 2,000, only one line of Cr (the raie ultime 4,254.34 A) was recognized as an impurity and omitted from the final list.

The identification of the raie ultime of rhenium is of considerable practical importance because there is no doubt that such a line constitutes the most sensitive test for rhenium that can be found. The Noddacks [16] assert that the optical spectrum is sensitive to $10^{-7}$ while the Röntgen spectrum can not detect rhenium in concentrations of less than $2 \times 10^{-4}$. Examination of 1,600 minerals from all parts of the world has revealed [17] Re in 100 of them, but never more than 0.001 per cent or $10^{-5}$. This explains why all attempts to detect Re in minerals by means of Röntgen rays failed [18] until the Noddacks conceived the plan of first enriching by chemical processes the concentration which might be expected in certain minerals. It accounts also for the entire absence of rhenium spectrum lines from tables of the characteristic spectra of other chemical elements. Comparison with the arc spectrum tables of Exner and Haschek,[19] which are the most complete with reference to faint lines, fails to disclose any coincidences with the sensitive lines of rhenium in any of the following: Mo, Mn, Nb, Ru, Pd, Pt, Rh, Os, Ir, W, Ta. This is quite different from the case of hafnium which was readily identified by recognition of its Röntgen spectrum in ordinary zirconium minerals and was later found to have been represented for many years by hundreds of lines [20] in the emission spectrum tables ascribed to zirconium. The natural concentration of hafnium in zirconium ores averages several per cent, while no ores contain more than 0.001 per cent of rhenium, so that the difference in behavior is due to great disparity in concentration and not to a great difference in optical sensitivity of the characteristic spectrum lines.

The raie ultime of Mn is 4,030.76 A and the corresponding line of Re 3,460.47 A must be expected to be the most persistent one. Recent experiments in which the partial spectra of Re were photographed when Re metal powder was progressively diluted with powdered Mn confirm the supersensitiveness of this ultra-violet Re line; it reveals the presence of Re in Mn when the number of Re atoms is only 1 per 1,000,000 ($10^{-6}$), and according to Noddack it indicates the presence of Re in minerals even when the concentration is as low as $10^{-7}$. In some earlier tests of Re concentrations in Mo and other metals it was invariably found that the blue Re line (4,889.15 A) was the most intense, and this deceived the writer at first into believing that this line was the true raie ultime analogous to Mn 4,030.76 A. Later experience, however, has shown that the blue line has superior intensity only when the concentration of Re is 0.1 per cent or more; with progressive dilution the ultra-violet line (3,460.47 A) persists after 4,889.15 A has vanished.

The structures of the rhenium spectra are expected to resemble those of the corresponding manganese spectra, although large departures from the LS coupling may occur, entailing violations of the interval rules and normal intensity formulas. The only spectrum of

[16] Ida Noddack, Zeitschr. Elektrochem., **34**, p. 629; 1928.
[17] I. and W. Noddack, Metallborse, **20**, p. 621; 1930.
[18] Bansanquet and Keeley, Phil. Mag., **48**, p. 845; 1924.
[19] Exner and Haschek, Bogen Spektren der Elemente, Deutike, Leipzig; 1911.
[20] W. F. Meggers, B. S. Jour. Research, **1** (RP 8), p. 151; 1928.

an adjacent element with which that of rhenium may be compared is the arc spectrum of tungsten which has been partially analysed by Laporte.[21] In this case a low energy $^5D$ term and a higher $^5P$ term have been identified, both are regular, but deviate widely from the interval rule. The most complete analysis and interpretation of the first spectrum of manganese is found in the work of McLennan and McLay,[22] and of Russell.[23] The normal state of the neutral Mn atom is represented by a $^6S$ term arising from the $d^5s^2$ configuration of its 7 valence electrons. Higher metastable terms appear as $(d^6s)$ $^4D$ and $(d^6s)$ $^6D$, both of which are regular. The configuration $d^5sp$ gives rise to one $^4P°$ term, two $^6P°$ terms and one $^8P°$ term, all of which are inverted except $^4P°$. In all of the above-mentioned complex terms the interval rule is adhered to qualitatively.

TABLE 2.—*Energy levels of the rhenium atom*

| Level No. | Value | J | Identification | Level No. | Value | J | Identification |
|---|---|---|---|---|---|---|---|
| 1 | 0.00 | 2½ | $a^6S$ | 46 | 38, 904. 65 | 4½ | |
| 2 | 11, 583. 91 | 2½ | | 47 | 39, 064. 90 | 2½ | |
| 3 | 11, 754. 49 | 4½ | $^6D$ | 48 | 39, 196. 67 | 5½ | |
| 4 | 12, 251. 22 | 1½? | | 49 | 39, 552. 34 | 4½ | |
| 5 | 13, 826. 07 | 1½ | | 50 | 39, 655. 81 | 4½ | |
| 6 | 14, 216. 80 | 3½ | $^6D$ | 51 | 39, 670. 42 | 2½ | |
| 7 | 14, 434. 03 | 4½ | | 52 | 39, 844. 68 | 3½ | |
| 8 | 14, 621. 37 | 2½ | | 53 | 39, 916. 29 | 4½ | |
| 9 | 15, 058. 10 | 3½ | | 54 | 40, 493. 54 | 5½ | |
| 10 | 15, 770. 27 | 2½ | $^6D$ | 55 | 40, 808. 77 | 1½ | |
| 11 | 16, 307. 02 | 5½ | $^4G$? | 56 | 40, 810. 05 | 1½ | |
| 12 | 16, 327. 41 | 1½ | $^6D$ | 57 | 40, 821. 72 | 2½ | |
| 13 | 16, 619. 12 | 4½ | $^4G$? | 58 | 40, 946. 47 | 3½ | |
| 14 | 17, 238. 21 | 0½ | $^6D$ | 59 | 40, 997. 54 | 4½ | |
| 15 | 17, 330. 71 | 3½ | | 60 | 41, 163. 83 | 3½ | |
| 16 | 17, 695. 29 | 2½ | | 61 | 41, 312. 95 | 2½ | |
| 17 | 18, 950. 15 | 2½ | $z^8P°$ | 62 | 41, 453. 14 | 4½ | |
| 18 | 20, 447. 76 | 3½ | $z^8P°$ | 63 | 41, 556. 95 | 1½ | |
| 19 | 21, 775. 30 | 3½ | | 64 | 41, 843. 78 | 3½ | |
| 20 | 23, 631. 80 | 4½ | $z^8P°$ | 65 | 42, 139. 99 | 4½ | |
| 21 | 28, 854. 15 | 2½ | $z^6P°$ | 66 | 42, 536. 29 | 3½ | |
| 22 | 28, 889. 64 | 3½ | $z^6P°$ | 67 | 42, 598. 33 | 3½ | $e^6S$ |
| 23 | 28, 961. 51 | 1½ | $z^6P°$ | 68 | 43, 341. 84 | 1½ | |
| 24 | 32, 443. 57 | 0½ | | 69 | 43, 407. 82 | 3½ | |
| 25 | 32, 591. 51 | 1½ | | 70 | 43, 409. 06 | 1½? | |
| 26 | 33, 408. 70 | 2½ | | 71 | 43, 453. 32 | 4½ | |
| 27 | 33, 410. 63 | 0½ | | 72 | 43, 569. 36 | 2½ | |
| 28 | 33, 589. 08 | 1½ | | 73 | 43, 702. 14 | 1½ | |
| 29 | 33, 898. 08 | 1½? | | 74 | 43, 800. 57 | 3½ | |
| 30 | 34, 445. 33 | 1½? | | 75 | 44, 054. 15 | 2½ | |
| 31 | 34, 520. 21 | 3½ | | 76 | 44, 224. 54 | 4½ | |
| 32 | 34, 818. 59 | 2½ | | 77 | 44, 308. 61 | 2½ | |
| 33 | 35, 129. 25 | 1½ | | 78 | 44, 703. 38 | 2½ | $e^4S$ |
| 34 | 35, 267. 84 | 2½ | | 79 | 44, 901. 06 | 3½ | |
| 35 | 35, 751. 23 | 0½ | | 80 | 44, 902. 50 | 2½ | |
| 36 | 35, 922. 94 | 4½ | | 81 | 45, 082. 59 | 5½? | |
| 37 | 37, 063. 57 | 1½ | | 82 | 45, 343. 49 | 4½ | |
| 38 | 37, 381. 30 | 1½, 3½ | | 83 | 45, 462. 76 | 3½ | |
| 39 | 37, 697. 62 | 2½ | | 84 | 45, 937. 16 | 3½ | |
| 40 | 37, 765. 53 | 3½ | | 85 | 46, 112. 20 | 2½ | |
| 41 | 37, 915. 84 | 1½ | | 86 | 46, 141. 02 | 1½ | |
| 42 | 38, 018. 92 | 0½ | | 87 | 46, 352. 94 | 3½ | |
| 43 | 38, 224. 64 | 1½ | | 88 | 46, 374. 21 | 4½ | |
| 44 | 38, 520. 58 | 3½ | | 89 | 46, 509. 33 | 2½ | |
| 45 | 38, 635. 35 | 0½ | | 90 | 46, 649. 36 | 2½ | |

[21] O. Laporte, Naturwissenschaften, **13**, p. 627; 1925.
[22] J. C. McLennan and A. B. McLay, Trans. Roy. Soc. Can., **3**, p. 89; 1926.
[23] H. N. Russell, Astrophys. J., **66**, pp. 283; 347; 1927.

TABLE 2.—*Energy levels of the rhenium atom*—Continued

| Level No. | Value | J | Identification | Level No. | Value | J | Identification |
|---|---|---|---|---|---|---|---|
| 91 | 47,004.13 | 1½ | | 106 | 50,359.19 | 3½ | $e^6D$ |
| 92 | 47,205.66 | 4½ | | 107 | 50,395.60 | 4½ | $e^6D$ |
| 93 | 47,668.98 | 3½ | | 108 | 50,464.54 | 5½ | $e^6D$ |
| 94 | 47,859.87 | 5½? | | 109 | 50,934.03 | 2½ | |
| 95 | 47,899.18 | 2½ | | 110 | 50,973.02 | 1½ | |
| 96 | 47,932.43 | 3½ | | 111 | 50,988.39 | 3½ | $e^6D$ |
| 97 | 47,970.73 | 2½ | | 112 | 50,994.12 | 4½ | $e^6D$ |
| 98 | 48,184.10 | 3½ | | 113 | 51,030.79 | 1½ | |
| 99 | 48,569.38 | 0½ | | 114 | 51,035.48 | 2½ | |
| 100 | 49,022.70 | 2½ | | 115 | 53,392.20 | 3½ | $f^8S$ |
| 101 | 49,027.85 | 2½? | | | | | |
| 102 | 49,274.89 | 3½ | | | | | |
| 103 | 50,110.22 | 2½ | | | | | |
| 104 | 50,332.62 | 1½ | $e^6D$ | | | | |
| 105 | 50,340.64 | 2½ | $e^6D$ | | | | |

TABLE 3.—*Multiplets in the $Re_I$ spectrum*

| | $z^8P_{3½}$ 28,889.64 | $z^8P_{2½}$ 28,854.15 | $z^8P_{1½}$ 28,961.51 |
|---|---|---|---|
| $a^6S_{2½}$ 0.00 | 3,460.47 (1,000) 28,889.57 | 3,464.72 (800) 28,854.13 | 3,451.88 (600) 28,961.45 |
| $a^6D_{4½}$ 11,754.49 | 5,834.31 (500) 17,135.25 | | |
| $a^6D_{3½}$ 14,216.80 | 6,813.42 (200) 14,672.87 | 6,829.96 (200) 14,637.35 | |
| $a^6D_{2½}$ 15,770.27 | 7,620.20 (60) 13,119.41 | 7,640.92 (200) 13,083.81 | 7,578.70 (100) 13,191.25 |
| $a^6D_{1½}$ 16,327.41 | | 7,980.70 (50) 12,526.79 | 7,912.90 (80) 12,634.12 |
| $a^6D_{0½}$ 17,238.21 | | | 8,527.68 (40) 11,723.30 |
| $e^6S_{2½}$ 44,703.38 | 6,321.89 (120) 15,813.69 | 6,307.71 (100) 15,849.24 | 6,350.75 (80) 15,741.83 |
| | $z^8P°_{4½}$ 23,631.80 | $z^8P°_{3½}$ 20,447.76 | $z^8P°_{2½}$ 18,950.15 |
| $a^6S_{2½}$ 0.00 | | 4,889.15 (2,000) 20,447.76 | 5,275.54 (1,000) 18,950.15 |
| $e^6S_{2½}$ 42,598.33 | 5,270.96 (500) 18,966.61 | 4,513.31 (300) 22,150.50 | 23,648.28 (200) 23,648.28 |
| $e^6D_{3½}$ 50,464.54 | 3,725.76 (100) 26,832.56 | | |
| $e^6D_{4½}$ 50,395.60 | 3,735.33 (50) 26,763.81 | 3,338.18 (60) 29,947.86 | |
| $e^6D_{3½}$ 50,359.19 | 3,740.41 (5) 26,727.47 | 3,342.25 (30) 29,911.39 | 3,182.87 (25) 31,409.14 |
| $e^6D_{2½}$ 50,340.64 | | 3,344.33 (30) 29,892.79 | 3,184.75 (50) 31,390.59 |
| $e^6D_{1½}$ 50,332.62 | | | 3,185.56 (40) 31,382.61 |

Now, in the first spectrum of rhenium there are five lines of outstanding intensity; these are as follows: 3,451.88 (600), 3,460.47 (1,000), 3,464.72 (800), 4,889.15 (2,000), 5,275.54 (1,000). The first three undoubtedly represent the transition, $(d^5s^2)a^6S-(d^5sp)z^6P°$, and the last two represent the transition $(d^5s^2)a^6S-(d^5sp)z^8P°$. With this

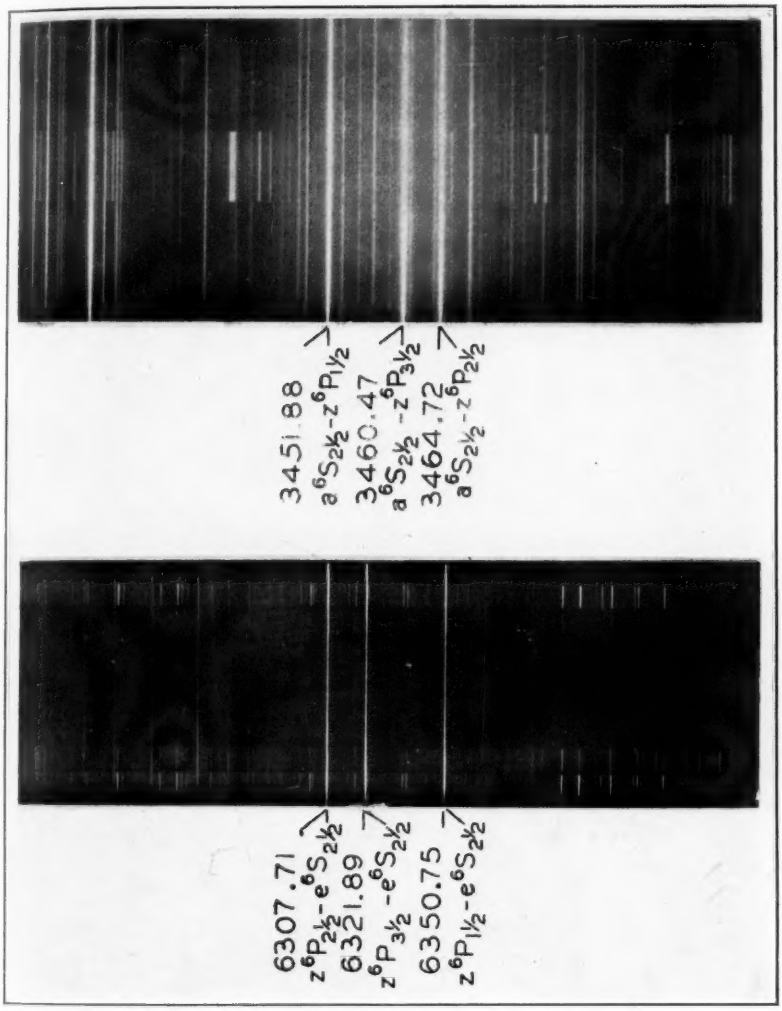


FIGURE 1.—*Two enantiomorphic triplets in the arc spectrum of rhenium, representing combinations of the threefold term, $z^6P$, with two successive single levels, $a^6S$ and $e^6S$, the first corresponding to the normal state of the neutral atom and the second to a more highly excited state than $z^6P$*

The first triplet contains the raie ultime (3,460.47 A) of Re. Narrow strips of the iron arc spectrum are superposed.

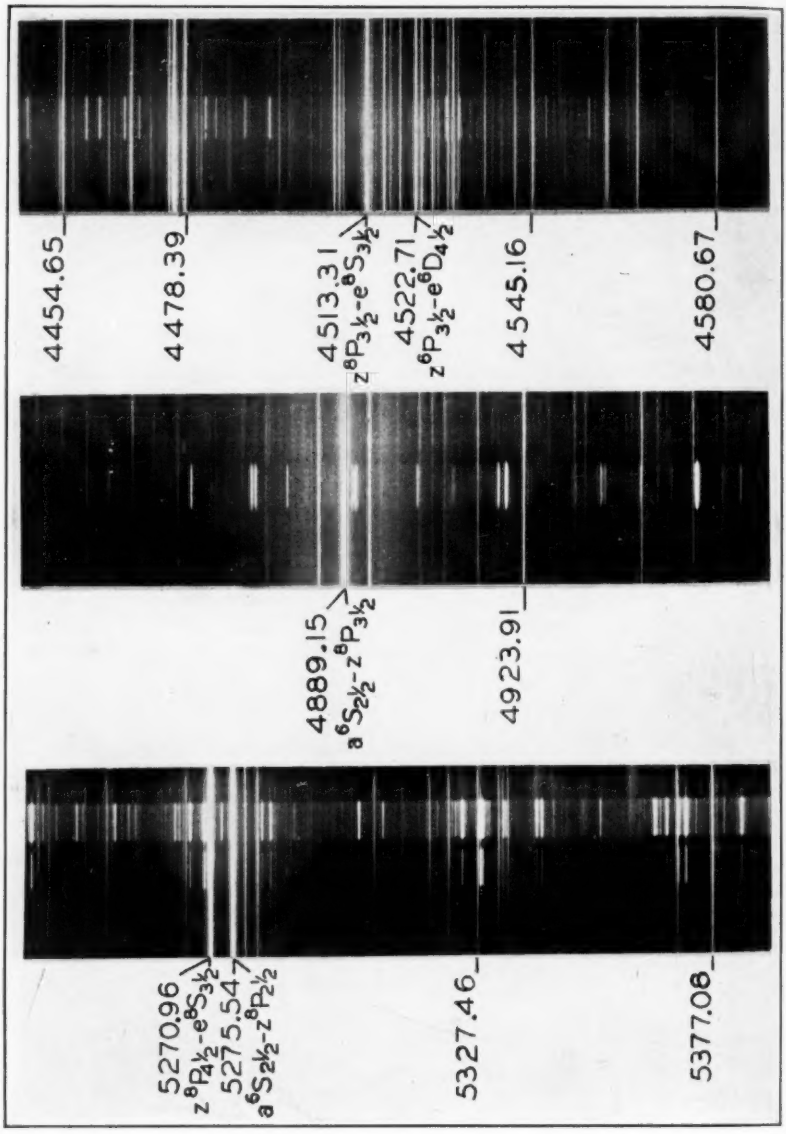


FIGURE 2.—*Portions of the visible spectrum of rhenium, including the resonance lines (4,889.15 and 5,275.54 A) and other combinations of terms belonging to sextet and octet systems*

Narrow strips of the iron arc spectrum are superposed.

clue to the structure of the spectrum and with the aid of numerous red and infra-red lines with wave number differences of the $z^6P°$ term it was easy to establish a considerable number of levels between 11,583.8 and 21,885.3 wave number units above the ground level. The combinations of these with still higher levels account for about 500 rhenium lines, including practically all of those with intensity greater than 20, on a scale ranging from 1 to 2,000. It is to be observed that $z^6P°$ is partially inverted and does great violence to the interval rule. Under these circumstances there does not appear to be any way at present to identify all of the remaining levels and group them with certainty into complex terms. Only the relative values and inner quantum numbers of the levels can be fixed; the combinations can be symbolized conveniently by representing the levels by serial numbers in order of increasing magnitude reckoned from zero for the ground state or level $1 = {}^6S_{2½} = 0$. The relative values of the levels thus symbolized in column 4 of Table 1 are collected in Table 2, column 2; the serial number of the term appears in the first column, the inner quantum number in the third and suggested identification of some of the levels is given in the fourth. The number of levels and, perhaps, also the identification of them can be easily extended when the spectrum has been satisfactorily observed in the interval between 2,000 and 2,500 A. A number of the principal multiplets in the $Re_I$ spectrum are shown in Table 3, and some of the lines are reproduced in Figures 1 and 2.

In very complex spectra, such as the one under discussion, it is very difficult to find extended series of spectral terms. Only in simple spectra, where the terms are single or double levels, are long series developed (especially in absorption), but in spectra with terms of higher multiplicity it is not easy to establish the second member of a series and it is very rare that a third member is found. The combinations from successive higher series terms in these complex spectra are always faint lines and frequently of a diffuse character. Furthermore, one must be on guard against fortuitous constant differences in these complex spectra because the number of lines is large enough to find successive pairs of lines with any desired wave number separation.

As stated before, the arc spectrum of rhenium is expected to resemble that of manganese, and two series were detected in the latter by Kayser and Runge [24] as long ago as 1894. These are now interpreted as the series $z^8P° - n^8S$ and $z^8P° - n^8D$. From these series the absolute values of $z^8P°$ can be calculated, and then by addition of the intersystem combinations $a^6S - z^8P°$ the value of the term $a^6S$ describing the normal state of the atom is arrived at. A similar procedure is possible with rhenium on the basis of two triplets interpreted as combinations of $z^8P°$ with successive $^8S$ series terms. The wave numbers and combinations are as follows:

| Wave number | Combination |
|---|---|
| 18, 966. 61 (500) | $z^8P°_{4½} - e^8S_{3½}$ |
| 22, 150. 50 (300) | $z^8P°_{3½} - e^8S_{3½}$ |
| 23, 648. 28 (200) | $z^8P°_{2½} - e^8S_{3½}$ |
| 29, 760. 38 (4) | $z^8P°_{4½} - f^8S_{3½}$ |
| 32, 944. 47 (5) | $z^8P°_{3½} - f^8S_{3½}$ |
| 34, 442. 99 (20)? | $z^8P°_{2½} - f^8S_{3½}$ |

[24] H. Kayser and C. Runge, Abh. Berl. Akad.; 1894.

Unfortunately the last line appears to be masked by another. The use of a Rydberg interpolation table on these lines leads at once to the following approximate values for $z^8P^\circ$ levels:

$$z^8P^\circ_{4\frac{1}{2}} = 39{,}898$$
$$z^8P^\circ_{3\frac{1}{2}} = 43{,}082$$
$$z^8P^\circ_{2\frac{1}{2}} = 44{,}580$$

Now this $z\ ^8P^0$ term is connected with the ground state by two intersystem combinations of outstanding intensity; they are represented as follows:

| Wave number | Combination |
|---|---|
| 20,447.76 (2000) | $a^6S_{2\frac{1}{2}} - z^8P^\circ_{3\frac{1}{2}}$ |
| 18,950.15 (1000) | $a^6S_{2\frac{1}{2}} - z^8P^\circ_{2\frac{1}{2}}$ |

and lead to the following values for the $a^6S_{2\frac{1}{2}}$ term:

$$a^6S_{2\frac{1}{2}} = z^8P^\circ_{3\frac{1}{2}} + (a^6S_{2\frac{1}{2}} - z^8P^\circ_{3\frac{1}{2}}) = 43{,}082 + 20{,}448 = 63{,}530$$
$$a^6S_{2\frac{1}{2}} = z^8P^\circ_{2\frac{1}{2}} + (a^6S_{2\frac{1}{2}} - z^8P^\circ_{2\frac{1}{2}}) = 44{,}580 + 18{,}950 = 63{,}530$$

This value of the deepest term in the $Re_I$ spectrum corresponds to an ionization potential of 7.85 volts.

It is a pleasure to acknowledge the assistance of Bourdon F. Scribner with the wave-length calculations, and the advice of Prof. Henry Norris Russell as to the interpretation of the spectral terms.

WASHINGTON, April 20, 1931.

# PURIFICATION AND ANALYSIS OF ALKALI CYANIDES

By M. R. Thompson

ABSTRACT

This paper summarizes the results of other investigators on the laboratory preparation of alkali cyanides of high purity, and considers several volumetric methods which have been used for the analysis of the product. Particular attention is given to the titrations with mercuric chloride (Hannay), nickel sulphate (Lundell) and silver nitrate (Liebig-Denigès).

In the present work, potassium and sodium cyanides were synthesized from liquid hydrocyanic acid and the appropriate hydroxide or ethoxide in ethyl alcohol solution. No difficulty was found in thus producing potassium cyanide of high purity, but the sodium cyanide was always less pure. This difference was traced to the reactions and solubility relations for potassium and sodium salts in ethyl alcohol. Methyl alcohol was found to be suitable for recrystallizing cyanides in certain cases, as the alkali salts are more soluble in it.

When applied to the pure potassium cyanide, the silver nitrate (Liebig-Denigès) method of analysis was found to be the most accurate.

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## I. INTRODUCTION

Alkali cyanide is an essential constituent of solutions used to electroplate with certain metals, including gold, silver, copper cadmium, zinc, and their alloys. The present commercial standard of purity is from 94 to 96 per cent for potassium cyanide and 96 to 98 per cent for sodium cyanide. "Chemically pure" material appears to be merely a selected grade of the above. The most common impurities are moisture, carbonate, cyanate, chloride, formate, and cyanamide.

More extensive knowledge is needed on the properties and control of the cyanide plating baths, and lately there has been a marked increase in research in this field. Although alkali cyanide of the above purity is quite adequate for commercial use, there are cases in research when small amounts of purer material are required. One example is the determination of the accuracy of analytical control methods.

Credit for very early achievements in the purification of potassium cyanide from ethyl alcohol solution should undoubtedly be given to Rogers and Rogers (1)[1] and to Wiggers (2), although unfortunately no analyses of the products were published. Later investigators used various methods of purification or synthesis and reported analyses. Their methods and results are summarized in Table 1. It is evident from Table 1 that nonaqueous solvents have been preferred, in order to prevent hydrolysis and the decomposition of cyanide.

TABLE 1.—*Results on the preparation of pure alkali cyanides*

| No. | Date | Author | Product | Purity | Method of preparation | Method of analysis |
|---|---|---|---|---|---|---|
| | | | | *Per cent* | | |
| 1 | 1875 | Loughlin (6) | KCN | 99.2 | Crystallization from carbon disulphide. | Titration with $AgNO_3$. |
| 2 | 1882 | Joannis (8) | NaCN | 99.7 | Gaseous HCN and alcoholic NaOH. | Titration with $I_2$ (5). |
| 3 | 1917 | Bucher (19) | do | 99.9 | Distillation at 1,000° C | Titration with $AgNO_3$. |
| 4 | 1923 | Ingold (25) | do | 99.8 | Liquid HCN and aqueous NaOH. | Do. |
| 5 | 1926 | Guernsey and Sherman (29). | do | 99.95 | Liquid HCN and alcoholic NaOH. | Titration with $NiSO_4$ (16). |
| 6 | 1926 | Hackspill and Grandadam (30). | KCN | 100.0 | Crystallization from liquid $NH_3$. | Titration with $AgNO_3$. |
| | | | NaCN | 100.0 | | |
| 7 | 1927 | Strachan [1] | do | 100.0 | Liquid HCN and alcoholic Na (ethoxide). | Do. |
| 8 | 1931 | Thompson [2] | KCN | 99.85 | Liquid HCN and alcoholic hydroxide. NaCN recrystallized from alcohol. | Titration with $AgNO_3$ from weight burette, using NaOH and KI indicator. |
| | | | NaCN | 99.43 | | |
| | | | do | 99.13 | Liquid HCN and alcoholic Na (ethoxide). | |

[1] Private communication from E. K. Strachan, Brown University, Providence, R. I.
[2] This paper.

Investigators have usually preferred the method of analysis which is the basis of all exact work with cyanides, namely, titration with standard silver nitrate solution. This appears to have been first described by Glassford and Napier (3), in 1844, but the papers of Liebig (4) in 1851 and 1852 attracted more attention and the method has always been inseparably associated with his name. Very important improvements, consisting in the addition of potassium iodide and an alkali, were described by Denigès (10) and by Sharwood (11). The accuracy has been studied from the aspect of the effects of large amounts of impurities, by Clennell (13), Burt-Gerrans and Morrison (15), Dott (18) and Sanigar (33); by comparison with other analytical methods, by Lundell (16), Frary and Porter (17), and Morris (22); and with relation to solubility determinations, by Bassett and Corbet (26).

The accuracy of the Liebig titration of cyanide has been questioned by Clevenger and Hall (14), who found certain results to be apparently 16 per cent low; but made no extensive investigation of the discrepancy; and by Frary and Porter (17), who compared the results with those by the mercuric chloride titration of Hannay (7). Frary and Porter found that the Liebig method gave results about 3 per cent lower than the Hannay method, when applied to their sample of potassium cyanide. They also believed that Liebig himself

[1] The figures given in parentheses here and throughout the text relate to the reference numbers in the bibliography given at the end of this paper.

doubted the accuracy of his method. A careful study of Liebig's text, however, leads to the conclusion that he referred to the disappointingly low purity of the product of his manufacturing process and not to any recognized error in the analytical procedure used for determining this purity.

The history of the preparation of "pure" cyanide shows many instances of difficulties in repeating previous work, which difficulties have led to the development of new or modified procedures. Reasons for this situation may include lack of knowledge of the exact technique required, use of different analytical methods, and the instability of cyanogen compounds.

## II. EXPERIMENTAL WORK

The experimental work of this investigation included a study and comparison of (*a*) methods of handling and analyzing samples of alkali cyanide, (*b*) methods of purifying alkali cyanide by recrystallization from organic solvents, and (*c*) methods of synthesizing pure alkali cyanide from liquid hydrocyanic acid. Commercial cyanide was used in exploratory experiments not reported here.

### 1. METHODS OF HANDLING AND ANALYZING SAMPLES OF ALKALI CYANIDE

Moisture or alcohol was removed by drying for two or three days in a desiccator over phosphorus pentoxide, applying a vacuum when necessary. A carbon dioxide absorbent, such as "ascarite" (sodium hydroxide on asbestos), was also kept in the desiccator. Drying in an electric oven at 100° to 125° C. for several hours also gave good results, provided that reasonable precautions were used to exclude carbon dioxide.

Carbonate was occasionally determined, by precipitating cold with barium chloride and titrating the barium carbonate obtained. Cyanide was ordinarily determined by the modified Liebig titration, adopting as standard conditions; 0.1 *N* silver nitrate, 10 ml of "indicator" solution containing 0.05 *N* potassium iodide and 0.25 *N* sodium hydroxide, a final titration volume of about 100 ml, room temperature and vigorous stirring. The purer samples were dissolved in the 10 ml of alkaline indicator before diluting, in order to decrease the possible loss of hydrocyanic acid. Volumetric burettes were used for work of ordinary accuracy (0.2 to 0.3 per cent) and weight burettes when higher accuracy (0.1 per cent) was required.

Comparison with other volumetric methods for cyanide was obtained in a few cases by using the nickel sulphate titration of Lundell (16) in which dimethylglyoxime is used as the indicator in the presence of a small amount of ammonia, or the mercuric chloride titration of Hannay (7). Results by the latter were always several per cent higher than by the silver nitrate titration. For example, an average purity of 103.4 per cent was obtained for the fairly pure potassium cyanide sample listed in Table 4. Similar results for less pure material were reported by Frary and Porter (17). In addition, it was found in the present work that the results varied according to the way the mercury solution was prepared and to the conditions used in the titration.

## 2. METHODS OF PURIFYING ALKALI CYANIDE BY RECRYSTALLIZATION FROM ORGANIC SOLVENTS

Recrystallization processes are attractive because of their simplicity and the avoidance of using the dangerous hydrocyanic acid. Organic solvents prevent or decrease the hydrolysis of cyanide and volatilization of hydrocyanic acid, which occur in aqueous solution. A suitable solvent should preferably (*a*) possess a considerable difference in solvent action on cyanide and impurities, (*b*) show but slight tendency to combine with cyanide directly or through condensation products, and (*c*) have either a marked temperature coefficient of solubility for cyanide, or else a conveniently low boiling point.

Attempts were made to use carbon disulphide as the solvent, according to the procedure of Loughlin (6), but without success. No appreciable amount of potassium cyanide, sodium cyanide, or the impurities contained in them, was dissolved at room temperature. Treatment of potassium cyanide with boiling carbon disulphide also gave negative results. Those of Loughlin are, therefore, difficult to explain.

Ethyl alcohol has been commonly used for dissolving cyanide, but methyl alcohol does not appear to have been considered. As few data were available on the solubility of cyanides and related salts in alcohols, some approximate determinations were made. These results and other published data are summarized in Table 2. Data on the solubility of cyanides in liquid ammonia have been given by Hackspill and Grandadam (30).

TABLE 2.—*Approximate solubilities of cyanides and related salts in alcohols at about 25° C.*

| Experiment | Salt | In ethyl alcohol, 95 per cent | In ethyl alcohol, absolute | In methyl alcohol, absolute |
|---|---|---|---|---|
| | | *g/liter* | *g/liter* | *g/liter* |
| 1 | KCN | 6.1 | 1.9 | 30.0 |
| 2 | KCN [1] (9) | | 6.9 | 39.2 |
| 3 | KCNO [2] (32) | | 2.2 | |
| 4 | $K_2CO_3$ | | 1.1 | 35.1 |
| 5 | NaCN | 19.2 | 9.7 | 78.0 |
| 6 | NaCNO [2] (32) | | 2.5 | |
| 7 | $Na_2CO_3$ | .05 | .02 | 2.1 |
| 8 | $Na_2CO_3$ [3] (21) | .24 | | |
| 9 | NaCOOH | 6.3 | | |

[1] Determinations at 19.5° C.
[2] Interpolated by M. R. T. from results with about 98 per cent alcohol.
[3] Determination at 30° C.

Recrystallization experiments were made with both alcohols. Difficulties were encountered both in precipitating cyanide by "freezing out" and by boiling off the alcohol. The best results were obtained by slowly evaporating the alcohol in a stream of inert gas at a moderate temperature. Some typical data are reported in Table 3.

TABLE 3.—*Effect of recrystallization from alcohol or extraction with alcohol upon the purity of alkali cyanides*

[All analyses were done by the Liebig titration, using KI-NaOH indicator]

| Experiment | Sample | Purity before | Purity after | Remarks |
|---|---|---|---|---|
| | | *Per cent* | *Per cent* | |
| 1 | NaCN made from HCN | 98.71<br>98.52<br>[1] 98.62 | 99.50<br>99.35<br>99.45<br>[1] 99.43 | Used absolute ethyl alcohol and evaporated at 35° to 40° C. in a stream of nitrogen or hydrogen. Slight gain in purity under preliminary conditions. Product showed 0.03 per cent moisture when dried at 125° C. Analyzed with weight burette. |
| 2 | NaCN (reagent quality) | 97.0 | 98.6 | Used absolute methyl alcohol and evaporated at about 20° C. in a stream of hydrogen. Much coloring matter present in solution at start and product grayer than original material. Very small scale work under preliminary conditions. |
| 3 | do | 97.2 | 97.3 | Used boiling absolute methyl alcohol in an extraction apparatus. No appreciable gain in purity. |
| 4 | KCN (reagent quality). | 93.4 | 97.8 | Used absolute methyl alcohol and evaporated at about 35° C. in a stream of hydrogen. Much coloring matter present in solution at start, but product was less yellow than original material. Distinct gain in purity, working on a very small scale under preliminary conditions. |
| 5 | Do | 96.2 | 96.8 | Used boiling absolute methyl alcohol in an extraction apparatus. Only a slight gain in purity. |

[1] Average.

## 3. METHODS OF SYNTHESIZING PURE ALKALI CYANIDE FROM LIQUID HYDROCYANIC ACID

Synthetic laboratory methods depend upon the use of hydrocyanic acid, usually liquefied for ease in handling and measurement. The solvent for the alkali is usually absolute ethyl alcohol, in which the alkali is dissolved either as hydroxide or as ethoxide (28). Such methods are more rapid and efficient than recrystallization.

Experiments were made mainly by the procedure which has been recently described in detail by Guernsey and Sherman (29). When a filtered solution of the appropriate hydroxide (40 g/liter) is treated with a 10 per cent excess of liquid hydrocyanic acid, alkali cyanide is formed and most of it precipitated.

$$NaOH + HCN = NaCN + H_2O$$

The unpublished method of E. K. Strachan [2] was also tried in which a solution of sodium in alcohol (40 g/l) is employed.

$$C_2H_5ONa + HCN = NaCN + C_2H_5OH$$

Hydrocyanic acid [3] was generated either in the apparatus described by Wade and Panting (12), or that by Ziegler (24). The former gave some difficulty from tar formation, which is a reaction discussed by Pelton and Schwarz (20) and by Harker (23). No such trouble was found with the Ziegler apparatus when properly adjusted, but the larger volume of liquid present interfered somewhat with the evolution of the hydrocyanic acid.

In alcoholic solutions there is a tendency toward the formation of brown "aldehyde resins," which may contaminate the product. The preliminary removal of traces of aldehyde by an appropriate method (27) did not always solve the problem. The effect is greater for sodium hydroxide than for potassium hydroxide, for sodium hydroxide than

[2] Private communication. See Table 1.
[3] Hydrocyanic acid boils at +25.7° C. and freezes at −14.9° C. The specific gravity of the liquid is 0.72 at 0° C.

for sodium cyanide, and for methyl alcohol than for ethyl alcohol. Useful measures include the use of low concentrations of alkali, stirring when the hydrocyanic acid is added and the removal of the precipitated cyanide as promptly as possible.

Data on the purity of synthetic potassium cyanide as determined by several methods are reported in Table 4 and similar data for sodium cyanide in Table 5.

TABLE 4.—*Determination of purity of potassium cyanide with weight burettes*

[The sample used throughout was synthesized from liquid HCN and KOH in absolute ethyl alcohol solution. It contained a negligible amount of sodium, amounting to 0.32 per cent, calculated as NaCN]

| Experiment | Method of analysis | Standard solution made from— | Analysis A | Analysis B | Analysis average | Remarks |
|---|---|---|---|---|---|---|
| | | | *Per cent* | *Per cent* | *Per cent* | |
| 1 | Liebig with no addition. | Weighed $AgNO_3$ crystals | 99.67 | 99.57 | 99.62 | Sample desiccator dried. Contained trace of $K_2CO_3$ by $BaCl_2$ test. Analysis done 9 weeks after preparation of sample. |
| 2 | Liebig with KI–NaOH. | ----do---- | 99.85 | 99.80 | 99.83 | Analysis done at same time as (1)[1]. Shows slightly higher and undoubtedly more accurate result because of use of KI–NaOH. |
| 3 | Do. | ----do---- | 99.73 | 99.76 | 99.75 | Similar to above, except done 10 weeks later. Difference probably due to change in sample, or in silver solution. |
| 4 | Do. | Weighed Ag shot | 99.86 | 99.84 | 99.85 | Sample desiccator dried. Analysis done at same time as (3). |
| 5 | Do. | ----do---- | 99.78 | 99.70 | 99.74 | Similar to above, except sample was both desiccator dried and dried at 110° C. Shows net loss in purity by latter drying. |
| 6 | Lundell | $NiSO_4.(NH_4)_2SO_4.6H_2O$ | 99.23 | | | Nickel solution was standardized by electro-analysis. |
| 6 | Do. | ----do---- | 99.29 | 99.44 | 99.32 | Sample desiccator dried. These analyses done 9 weeks after (1), or just before (3). |
| 7 | Do. | ----do---- | 99.47 | 99.56 | 99.52 | Sample dried both in desiccator and at 110° C. Analysis done at the same time as (6). Difference not due to moisture content (about 0.03 per cent). |

[1] Figures here and in tables refer to the experiment number.

TABLE 5.—*Determination of purity of sodium cyanide with weight burettes*

[The sample used in experiments 1–4 was synthesized from liquid HCN and NaOH in absolute ethyl alcohol solution. The sample used in experiment 5 was synthesized from liquid HCN and $C_2H_5ONa$ in absolute ethyl alcohol solution]

| Experiment | Method of analysis | Analysis A | Analysis B | Analysis average | Remarks |
|---|---|---|---|---|---|
| | | *Per cent* | *Per cent* | *Per cent* | |
| 1 | Liebig with no addition. | 98.38 | 98.52 | 98.45 | Sample desiccator dried. Contained about 0.8 per cent $Na_2CO_3$, by $BaCl_2$. Analysis done 8 weeks after preparation of sample. Silver solution for this experiment and also for experiments 2 and 3 was prepared from weighed $AgNO_3$ crystals. |
| 2 | Liebig with KI–NaOH. | 98.71 | 98.52 | 98.62 | Similar to above. Shows slightly higher and undoubtedly more accurate result because of use of KI–NaOH. Done at same time as (1). |
| 3 | ----do---- | 98.89 | 98.70 | 98.80 | Sample after drying in desiccator was fused in a nickel crucible under hydrogen. Shows only a slight gain in purity by fusion. Done soon after (1). |
| 4 | Lundell | 98.24 | 98.22 | 98.23 | Sample dried in desiccator and then at 110° C. Analysis done 6 weeks after (1). Nickel solution was prepared from nickel-ammonium sulphate and standardized by electro-analysis. |
| 5 | Liebig with KI–NaOH. | 99.16 | 99.10 | 99.13 | Sample dried in desiccator. Analysis done one week after preparation of sample. Contained less than 0.1 per cent $Na_2CO_3$, by $BaCl_2$. Drying at 125° C. did not increase purity. |

## III. DISCUSSION OF RESULTS

The synthetic potassium cyanide was considerably purer than the synthetic sodium cyanide, even after repeated attempts to improve the latter. This may be partly explained by the relatively high solubility of potassium carbonate in alcohol (Table 2), which tends to prevent contamination by this impurity. The sodium cyanide preparations usually contained an appreciable amount of carbonate, except the sample made by Strachan's procedure (Table 5, No. 5). In that experiment, the alcoholic solution was somewhat easier to filter and the Ziegler apparatus for generating hydrocyanic acid was supplied with a solution that had been freed from carbonate by treatment with barium hydroxide. This sample, however, still contained an appreciable amount of coloring matter. Further experience with Strachan's procedure would no doubt lead to better results.

The solubilities listed in Table 2 apply to separate salts, and in the case of mixtures may be altered by mutual solubility effects. No marked effects of this nature, however, were observed in the experiments.

The analyses of cyanide show slightly lower results by the Lundell than by the Liebig method (Tables 4 and 5), a difference similar to that reported by Lundell (16). In an attempt to explain this difference, the recrystallized nickel ammonium sulphate used was examined for cobalt. About 0.04 per cent of cobalt was found present (ratio of nickel to cobalt of about 400: 1), and the low result for cyanide must have been partly due to this impurity. The complete elimination of cobalt is therefore important if maximum accuracy is to be secured. At best, the conditions of the titration probably affect the end point to a greater extent than in the Liebig method, where it is also easier to obtain a pure salt for preparing the standard solution. The reaction taking place during the titration of cyanide with nickel solution is quite definite, however, as shown by the recent solubility determinations of Corbet (31).

The analytical results by the Liebig titration with silver nitrate (Tables 3, 4, and 5) make it evident that those of Frary and Porter (17) by this method must have been approximately correct and not about 3 per cent low, as they thought. None of their data on the silver solutions used for measuring electrode potentials need to be changed, as they employed the Liebig titration values.

## IV. CONCLUSIONS

1. The high accuracy of the modified Liebig method for titrating alkali cyanide with silver nitrate solution and iodide indicator is supported by: (*a*) The weight of the evidence from the literature; (*b*) the additional results obtained in this investigation, through the preparation of potassium cyanide of high purity. The error of the Liebig method, under best conditions, is probably less than 0.2 per cent and may even be less than 0.1 per cent.

2. It is more difficult to synthesize pure sodium cyanide than pure potassium cyanide, by adding liquid hydrocyanic acid to an ethyl alcohol solution of the hydroxide.

3. An alcoholic solution of sodium ethoxide has advantages over one of sodium hydroxide, for the synthesis of pure sodium cyanide, especially in eliminating carbonate as an impurity.

4. The Ziegler apparatus for generating hydrocyanic acid can be operated so as to eliminate carbon dioxide, while this is difficult to effect with the Wade and Panting apparatus.

5. More investigation is needed on the laboratory synthesis of pure alkali cyanide and especially of sodium cyanide. The favorable conditions should be defined more exactly and the technique better standardized. The elimination of organic impurities derived from condensation products (of either aldehyde or hydrocyanic acid) is particularly important.

6. Alkali cyanides and related salts are more soluble in methyl than in ethyl alcohol. For certain grades of cyanide, methyl alcohol is more suitable as a solvent for purification by recrystallization. For other grades, ethyl alcohol is more satisfactory. Recrystallization is at best, however, a slower and less efficient process than synthesis with liquid hydrocyanic acid.

7. It is recommended that, in future work on this subject, the silver nitrate titration with weight burettes be adopted as one method of analysis for determining and reporting the purity of alkali cyanide, in order to facilitate the comparison of results.

## V. ACKNOWLEDGMENTS

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WASHINGTON, APRIL 16, 1931.

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# A MULTIPLE MANOMETER AND PISTON GAGES FOR PRECISION MEASUREMENTS

By C. H. Meyers and R. S. Jessup

ABSTRACT

The paper describes a 15-atmosphere differential mercury manometer and a group of piston gages constructed and maintained at the National Bureau of Standards in connection with the determination of the thermodynamic properties of substances.

The differential mercury manometer consists of five U tubes connected in series. Oil, alcohol, and water have been used at different times to transmit the pressure from one U tube to the next, water being the most satisfactory. The temperature of the manometer is measured with a mercury-in-glass thermometer, the bulb of which has the same length as the U tubes. The manometer was found to be accurate within 1 part in 10,000.

Each piston gage consists of a hardened steel piston and cylinder mounted vertically in a cast-iron base in such a manner that the piston and its load may be rotated continuously. The design is such as to permit applying the weights above the piston and yet avoid eccentric loading.

The procedure for calculating pressures from observations with these instruments is described, and the corrections to be applied are discussed.

The piston gages were calibrated as absolute instruments by means of measurements of piston diameter and width of crevice and as secondary instruments by direct comparison with the mercury manometer. Slight irregularities in the forms of pistons and cylinders impair the accuracy of the absolute calibration. Secular changes in the steel necessitate recalibration from time to time if the accuracy of which the gages are capable, 1 part in 10,000, is to be maintained.

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## I. INTRODUCTION

A multiple column mercury manometer for measuring pressure differences up to 15 bars,[1] and a group of piston gages for measuring pressures up to 100 bars, have been constructed and maintained at the National Bureau of Standards in connection with the determination of the thermodynamic properties of substances.

[1] The term "bar" is used in this paper in accordance with the usage now internationally accepted; that is, to indicate a pressure of 1,000,000 dynes per square centimeter or about 0.96784 normal atmospheres. The term microbar is used to indicate a pressure of 1 dyne per square centimeter.

These gages have been repeatedly intercompared and the technique of their operation developed, the purpose being twofold: (1) To increase the accuracy of the measurement of pressure as one of the thermodynamic variables, (2) to investigate the reliability of the piston gage as a primary standard instrument.

## II. DESCRIPTION OF MANOMETER

The 15-bar manometer in its present form, as shown in Figure 1, is the result of a gradual development extending over a period of years. The original design, as developed by Dr. Edgar Buckingham, provided for an instrument for routine laboratory use, made so that

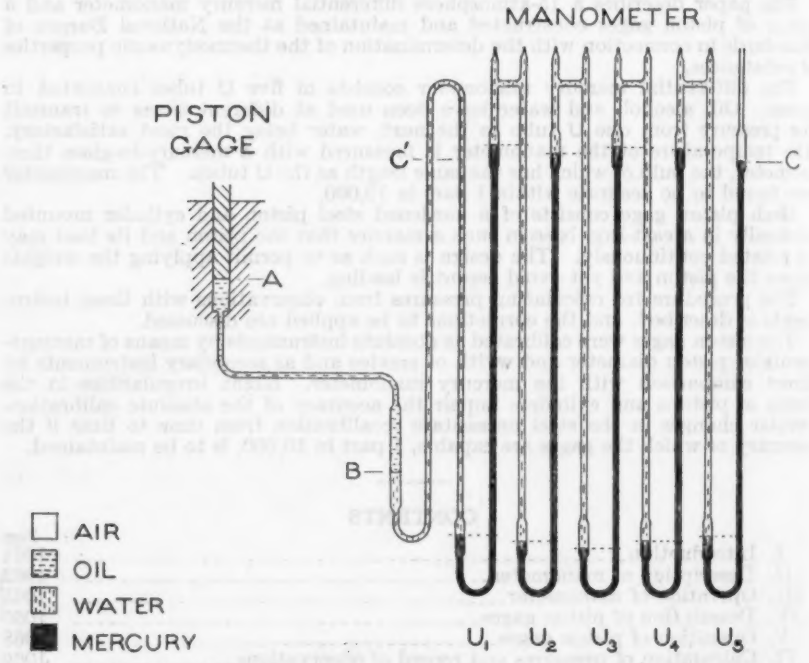


FIGURE 2.—*Schematic diagram of manometer connected to piston gage*

any pressure difference between zero and 15 bars could be measured. When it was found later that pressures as low as 1.2 bars could be measured much more conveniently and with equal accuracy with a piston gage, the manometer became merely a standard for the calibration of the piston gages. When used for this purpose, measurements at intervals of three bars were ample, and the design of the manometer was greatly simplified by the omission of glass-to-metal joints, valves, etc. These changes served to eliminate many points at which leakage could occur, removed possible sources of fouling of the mercury, simplified the manipulation, and increased the dependability without sacrificing anything except the possibility of measuring every pressure within its range.

Liquid with a low or moderate vapor pressure was chosen in preference to gas for transmitting the pressure from one U tube to the

FIGURE 1.—*Photograph of manometer and piston gage*

OF MICH.

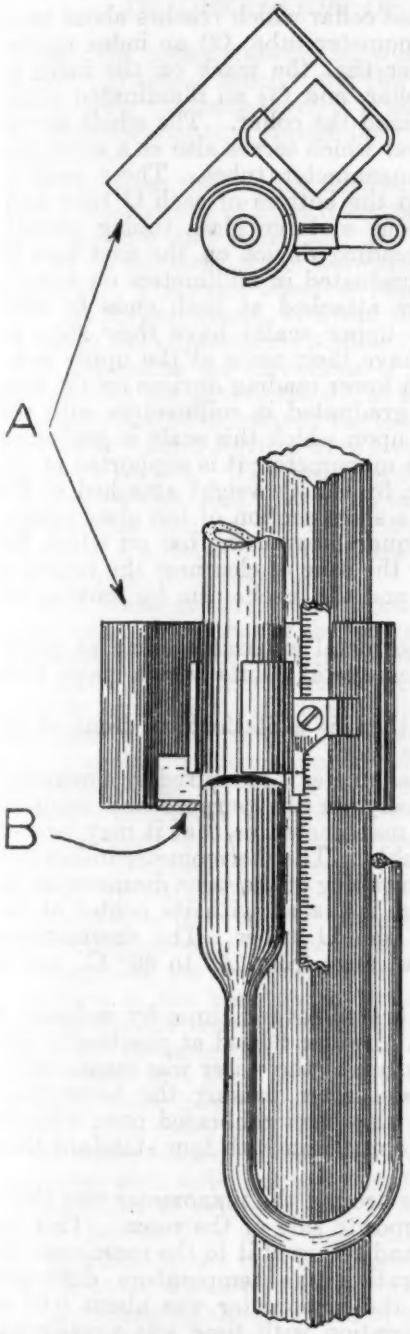


FIGURE 3.—*Reading device for manometer*

(*a*) Housing for electric lamp.
(*b*) Illuminated background.

next, because the use of liquid offers less danger from flying glass in case of rupture, and simplifies the adjustment of the manometer. Oil, specially purified absolute alcohol, and distilled water have been used for this purpose. The use of oil proved unsatisfactory because of its action upon mercury; the latter became badly fouled and even emulsified. The use of alcohol was also unsatisfactory; the mercury became slightly fouled, and occasional redeterminations of the density of the alcohol were necessary, due to the absorption of moisture. The use of water, possible only after the omission of certain metallic parts, has given satisfactory results; the positions of the mercury surfaces were definite to within 0.05 mm.

As may be seen in the schematic diagram (fig. 2) the manometer consists of five glass U tubes about 2.5 m long connected in series. The instrument was designed in this manner so that it could be housed in a single room. The glass tubing is mounted in a rigid steel frame, each U tube being supported near the top by a clamp lined with soft rubber, and kept in alignment by loosely fitting clamps near the middle and the bottom. The glass tubing has an inside diameter of about 3 mm and a wall thickness of about 1 mm, except at places where readings are to be taken. At such places there are sections of tubing about 10 cm long having an inside diameter of about 10 mm and a wall thickness of about 2.5 mm. One of these sections is located near the bottom of the left-hand branch of each U tube and another near the top of the right-hand branch, as illustrated in Figure 2.

Figure 3 illustrates one of the reading devices for the manometer.

Each of these consists of (1) a brass collar which reaches about two-thirds of the way around the manometer tube, (2) an index rigidly fixed to the collar in such manner that the mark on the index is opposite the lower edge of the collar, and (3) an illuminated white background located below and behind the collar. The whole device slides on a vertical, square, steel bar which serves also as a mounting for the clamps supporting the manometer tubes. These reading devices are located at the top and the bottom of each U tube with the collars surrounding the sections of large glass tubing already mentioned. The index of each reading device on the first four U tubes bears upon a 10 cm scale graduated in millimeters on a short steel tape. These steel tapes are attached at both ends to their respective supporting rods. The upper scales have their zeros at the lower ends; the lower scales have their zeros at the upper ends. The indices of both the upper and lower reading devices on the fifth U tube bear upon a 2.8 m scale graduated in millimeters with the zero at the lower end. The tape upon which this scale is graduated extends over the full height of the manometer; it is supported at the upper end and kept under tension by a 2 kg weight attached at the lower end. Figure 3 shows only a short section of the glass tubing, of the divided scale, and of the square supporting bar on which the reading device slides; it omits for the sake of clearness the means of attaching the scale to its support and the mechanism for moving the reading device.

The manometer is connected to metal apparatus, such as piston gages, by means of soldered glass-metal joints which have been described elsewhere.[2] [3]

For convenience in operation, there is a platform in front of the manometer about 1.5 m above the floor.

The mean temperature of the manometer is measured by a mercury-in-glass thermometer made specially for the purpose and mounted vertically about 6 cm behind the manometer, so that it may be seen between the second and third U tubes. The thermometer bulb which is about 2.5 m long and made from tubing of the same diameter as the smaller tubing in the manometer, is placed with its center at the same elevation as the center of the U tubes. The thermometer scale, about 20 cm long, covers a range from 10° to 36° C., and is divided into intervals of 0.2° C.

The thermometer has been calibrated several times by inclosing it in a pipe through which a stream of water flowed at practically constant temperature. The temperature of the water was measured by standard thermometers before and after passing the termometer under test. The instrument has also been calibrated once while in place behind the manometer by comparison with four standard thermometers hanging beside it.

During all observations, the air around the manometer was circulated by a fan located on the opposite side of the room. This fan withdrew air from near the floor and returned it to the room near the ceiling. With this fan in operation the temperature difference between the top and bottom of the manometer was about 0.6° or 0.7° C., and the temperature variation with time was usually not more than 0.1° or 0.2° per hour.

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[2] McKelvy and Taylor, J. Am. Chem. Soc. **42**, p. 1364; 1920.
[3] Meyers, J. Am. Chem. Soc. **45**, p. 2135; 1923.

## III. OPERATION OF THE MANOMETER

With the present design in which all the U tubes have approximately the same capacity and the mercury in each is brought to approximately the same level, it is necessary to vary the amount of the pressure-transmitting liquid only at the high-pressure end of the manometer.

In adjusting the reading devices, the brass collar was lowered until only a faint streak of light from the illuminated background could be seen between the collar and the meniscus. The positions of the indices on the fixed scales were then read with the aid of a magnifying glass. The same observer read both ends of the manometer for any one measurement, to avoid the errors due to systematic difference in the adjustments made by different observers.

To determine the elevations of the zeros of the short scales with reference to the zero of the 2.8 m tape, a plane surface was leveled at a suitable height in front of the lower end of the manometer, the first four lower reading devices were lowered until the brass collars touched the plane surface. The positions of their indices were then read upon the short scales, and that of an index rigidly attached to the plane surface was read on the 2.8 m tape. The plane surface was then leveled at a suitable height in front of the upper end of the manometer and the procedure repeated.

From these readings the effective elevations of the zeros of the short scales above that of the long tape can be directly obtained when the vertical distance from the plane surface to the index attached to it is known, the effective elevation of a zero being that which when suitably combined with the reading of the index gives the actual elevation of the bottom of the associated collar. It differs from the true elevation by the amount by which the index is displaced from the the plane of the lower edge of its associated collar, and its use automatically eliminates the effect of such displacement.

But in each set of readings (upper or lower), the differences in the effective elevation of the zeros of the several short scales are given directly by the differences in the readings of their indices, entirely irrespective of the vertical distance from the plane surface to the index attached to it. Likewise, the effective vertical distance between the upper and the lower zero of any pair of short scales is given by the difference in the readings of the index on the long scale, suitably modified by the readings of the appropriate indices on the short ones. Again the distance from the plane surface to its index is a matter of indifference, and need not be known. It may be easily shown that the only place in which a knowledge of the distance from the plane surface to its index need be known is in the computation of the height of the water column in the manometer. This distance can easily be measured with sufficient accuracy for that purpose.

The effect of errors in the location of the indices of the reading devices for the fifth tube, was determined by using them to measure the positions of the mercury menisci in the two branches of a short open U tube, which temporarily replaced the fifth manometer tube. By interchanging the positions of the branches of this short U tube, any error due to a consistent difference in the capillary forces in the two branches was eliminated.

## IV. DESCRIPTION OF PISTON GAGES

The first 100-bar piston gage, as originally constructed, was designed by Drs. H. C. Dickinson and M. S. Van Dusen. Later, a motor-driven device for rotating the piston was added, and a 10-bar gage and another 100-bar gage constructed, both with a motor-driven rotating device.

The identification mark and diameter of each piston and cylinder, as well as the identification mark of each cast-iron base, are given in Table 1. Each base was made for the piston and cylinder opposite its number, but either of the 100-bar bases may be used with any one of the cylinders A, B, or C.

TABLE 1.—*Identification of pistons and cylinders*

| Piston | | | Cylinder | | | Cast-iron base No. |
|---|---|---|---|---|---|---|
| Mark | Material | Diameter | Mark | Material | Diameter | |
| | | *mm* | | | *mm* | |
| 100-BAR GAGES | | | | | | |
| 1 | Drill rod (carbon steel) | 11.297 | [1] A | | 11.300 | 12083 |
| 2 | Sanderson's special steel | 11.318 | $A_1$ | | 11.322 | |
| 3 | Drill rod (carbon steel) | 11.261 | B | | 11.264 | 30213 |
| 4 | Chrome steel | 11.269 | C | Chrome steel | 11.273 | |
| 10-BAR GAGE | | | | | | |
| 5 | | 35.675 | D | | 35.683 | 30778 |

[1] Before lapping to fit piston 2.

NOTE.—Since the parts are to some extent interchangeable, the gages will be identified in this paper by giving the identification mark of the piston, cylinder, and base in the order named; for example, 3–B–30213.

The 10-bar gage is illustrated partly in section in Figures 4 and 5; it is practically the same as the 100-bar gage with the exception of its larger piston and cylinder and slightly larger oil pump. A scale of centimeters is given along with the drawings to show the size of the gages.

The steel cylinder is held rigidly in the cast-iron base by a threaded ring (No. *26* in figs. 4 and 5). This cylinder is composed of two parts, a hardened steel bushing (*22*) and a soft steel jacket (*25*). The outside of the bushing and the inside of the jacket are ground to a force fit over the upper two-thirds of their length, but have about 0.2 mm clearance over the lower third. This part, as may be seen in Figure 4, is somewhat larger in diameter but due to the reduced scale the clearance is not visible. The lower end of the cylinder is closed by screwing on a steel cap (*27*). By this construction a shoulder is formed on the bushing which prevents that part from being displaced upward by the pressure, and the bushing is separated from the jacket at the place where strains are likely to occur in the latter due to screwing on the cap. The clearance between the lower portion of the bushing and jacket has been made small so that an inappreciable amount of air is entrapped when the gage is being filled.

The length of bearing surface between the piston and cylinder in each gage is about 7 cm.

All the pistons and cylinders are of steel, the kind of steel being stated, in so far as known, in Table 1. Piston No. 2 was furnace annealed and the others quenched and then drawn to about 300° C. The pistons and cylinders were ground to approximately the correct diameter and finished by lapping to uniform diameters, such that they fit together with very little clearance and yet do not seize when stationary.

The load, applied to the gage by placing weights upon the cap (*1*), is transmitted through a steel shaft (*5*) to a steel ball (*29*) near the bottom of the hollow piston.

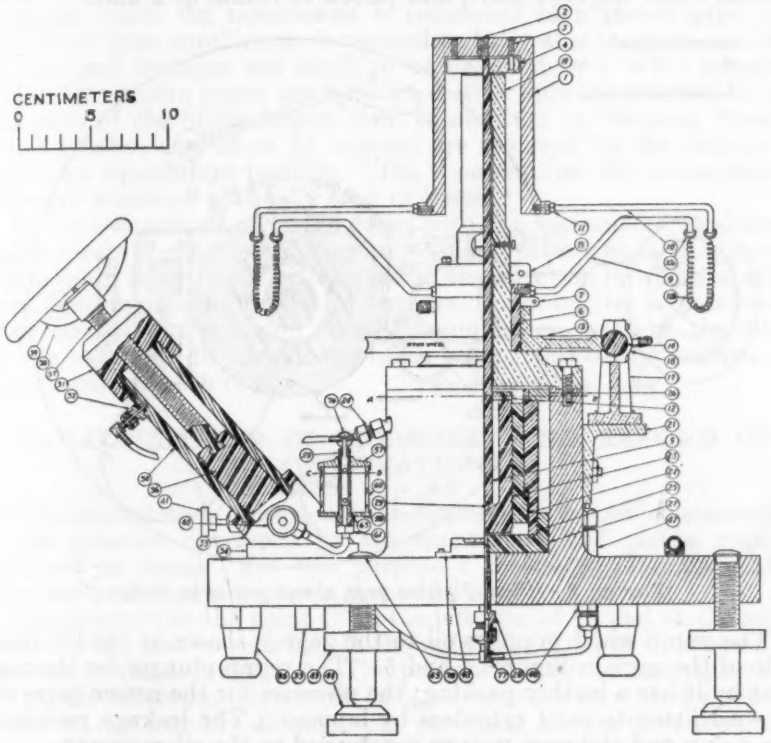


FIGURE 4.—*Elevation of piston gage, shown partly in section*

The temperature of each gage is measured by a mercury-in-glass thermometer (not shown in fig. 4 or 5) inserted in a hole in the cast-iron base in such manner that the thermometer bulb is at the same elevation as the center of the cylinder. The pressure to be measured is applied at the valve (*47*).

Frictional forces retarding the vertical motion of the piston are reduced by rotating the piston continuously in one direction. The rotation is produced by a small motor driving a worm gear (*13* and *14* in fig. 4). The adjustable friction clutch (*7*) drives a steel sleeve which carries a pair of arms (*9*). These arms are in turn connected through helical springs to another pair of arms mounted on the cap (*1*) in such manner that the ends of the two pairs are at the same height when the piston is about midway between the limits of its

vertical travel, in other words, at its normal position. The location of the piston may be determined by observation of the relative position of a mark on the shaft (*5*) and the point of a set screw mounted in the pedestal (*19*), both being visible through the sight hole shown in Figure 4 just below the cap (*1*). In certain pressure measurements where it was desired to observe the position of the piston very accurately, a miscroscope was used. The piston is at its normal position when the mark and point are at the same level. Two pins in the cap (*1*) which engage with two holes in the disk (*4*), and projections on the shaft (*5*) which engage with notches in the upper end of the piston, cause the cap, shaft, and piston to rotate as a unit.

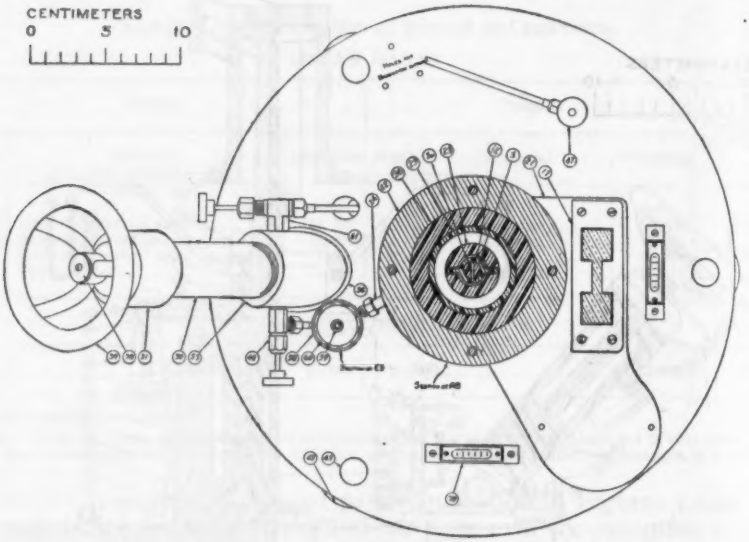


FIGURE 5.—*Plan of piston gage, shown partly in section*

The pump which supplies oil to the gage is shown at the left-hand side of the gage in Figures 4 and 5. The pump plunger for the gage first built has a leather packing; the plungers for the newer gages are of steel fitted to steel cylinders by lapping. The leakage past both the pump and the gage pistons is returned to the oil reservoir.

A short auxiliary mercury manometer is mounted on the cast-iron base. The purpose of this manometer is to separate the oil in the gage from the fluid, the pressure of which is to be measured. When the diameters of the manometer tubes are small, observation of the position of the mercury is a sensitive means of determining lack or presence of equilibrium. When it is unnecessary to use a separating device, or is more convenient to use a manometer mounted on other apparatus, the manometer and mounting on the gage may be removed.

## V. OPERATION OF PISTON GAGES

When a pressure is to be measured, the gage is leveled, the approximate required weight is placed on the gage, oil is pumped in until the piston is at its normal position, the piston is set in rotation, the valve

leading to the pressure to be measured is temporarily opened slightly, the velocity with which the piston moves up or down noted, and the weight adjusted accordingly. Failure to keep this valve closed causes no damage to the gage, since the piston travel is confined to narrow limits by stops; it may, however, cause the spilling of liquid from manometers connected to the gage if these manometers are of small capacity.

After the gage has been adjusted and the valve leading to the pressure has been opened wide, time is allowed for equilibrium to be attained. This period of time depends on the individual gage as well as on the conditions of observation and the precision required. For example, when the manometer is connected to a piston gage, the departure from equilibrium is reduced to half value in about one-half minute and becomes too small to be detected in 5 to 10 minutes. When two piston gages are connected with only oil between them, the ratio of the displacement from equilibrium to restoring force is much greater, and 15 or 20 minutes are required for the pistons to attain an equilibrium position. The time required for measurement of vapor pressures is equally long or longer.[4]

In the comparison of piston gages with the manometer, the observations were divided into two groups, approximately equal in number, the division being made with regard to the direction in which equilibrium was approached. One group was preceded by a downward displacement of the piston from the equilibrium position, the other by an upward displacement, time being allowed for return to equilibrium in both cases.

## VI. CALCULATION OF PRESSURES AND RECORD OF OBSERVATIONS

The description of the calculation of pressures is clarified somewhat if the pressure developed by the manometer and piston gage is analyzed in detail. For this purpose a schematic diagram of the manometer and piston gage is given in Figure 2.

The pressure at the point $C'$ in the left arm of $U_1$ and at the same height as the mercury surface in the right arm of $U_5$ at $C$, is equal to the sum of the following: (1) The pressure $At_c$ of the atmosphere at $C$; (2) the difference in pressure ($p_{cap}$) due to the combined capillary forces of the mercury-air meniscus at $C$ and all the mercury-water menisci in the manometer; and (3) the excess ($E$) of the pressure exerted by a mercury column of height ($H$), equal to the sum of the differences in level of the menisci bounding the several mercury columns, over that exerted by a water column of the same height.

The last item is easily visualized if one considers the path which starts at $C$ (fig. 2) and follows down the right side of $U_5$ to the short horizontal dotted line, thence along the dotted line and up the left side of $U_5$ to the upper dotted line, thence along that dotted line, down and so on to $C'$. Each dotted line intersects two tubes at points of equal pressure, the downward part of the path corresponds to an increase in pressure equal to the head of mercury in a column of height ($H$), and the upward part corresponds to a decrease in pressure equal to the head of water in a column of the same vertical

[4] Cragoe, Meyers, and Taylor, B. S. Sci. Papers, 16, p. 1; 1920. Sci. Paper No. 369.

height, since the path starts and ends at the same level, and consequently the downward and upward paths must be equal.

The pressure at $A$ is equal to that at $C'$ plus that of a water column of height $BC$ minus that of an oil column of height $BA$, the amount by which the level of $A$ exceeds that of $B$. If the densities of mercury, oil, and water are denoted, respectively, by $\rho_{Hg}$ $\rho_o$ and $\rho_w$ then the pressure at $A$ is

$$P_A = At_c + (p_{cap}) + \rho_{Hg}\, gH - \rho_w\, gH + \rho_w\, g\, BC - \rho_o\, g\, BA$$
$$= At_c + (p_{cap}) + g\{(\rho_{Hg} - \rho_w)\, H + \rho_w\, BC - \rho_o\, BA\} \quad (1)$$

This pressure acts upward at $A$ upon the piston of the pressure gage.

If the base of the piston were a horizontal plane, and if there were no leakage of oil past it, then when equilibrium exists this pressure ($P_A$) would equal the ratio of the force acting downward through the piston, to the area of the base of the piston. That force is equal to the atmospheric pressure ($At_A$) at the level $A$ times the area of the base of the piston, plus the weight ($W$) of the piston and the load it carries, corrected for the buoyancy of the atmosphere. Hence

$$P_A = At_c + (p_{cap}) + g\{(\rho_{Hg} - \rho_w)H + \rho_w BC - \rho_o h_o\} = At_A + \frac{Wg}{AREA} \quad (2)$$

or

$$AREA = Wg/[(At_c - At_A) + (p_{cap}) + g\{(\rho_{Hg} - \rho_w)H + \rho_w BC - \rho_o h_o\}] \quad (3)$$
$$= Wg/(P_A - At_A)$$

In the actual gages there is always some leakage of oil past the piston. This results in a lifting force on the piston, due to the viscous drag of the oil. This force is very closely proportional to the product of pressure times the cross-sectional area of the crevice between the piston and cylinder, and consequently its presence is equivalent to a slight increase in the radius of the piston. The area defined by this greater radius is called the effective area of the piston; it is the area that is defined by equation (3). The relation between the effective area and the actual area is considered later.

The observations made with the manometer during a comparison with a piston gage and the computation of pressure from these observations are given in Table 2.

TABLE 2.—*Record of pressure measurements with the manometer*

[Observer C. H. M. Computed by C. H. M. Date, March 2, 1928]

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Observed temperature | °C. | 21.90 | 22.00 | 22.15 | 22.15 | 22.20 | 22.30 | 22.30 | 22.30 | 22.35 |
| 2 | Corrected temperature | do. | 21.90 | 22.00 | 22.15 | 22.15 | 22.20 | 22.30 | 22.30 | 22.30 | 22.35 |
| 3 | Density of oil | | .890 | .890 | .890 | .890 | .890 | .890 | .890 | .890 | .890 |
| 4 | Density of water | | .9978 | .9978 | .9978 | .9978 | .9978 | .9977 | .9977 | .9977 | .9977 |
| 5 | Density (Hg minus $H_2O$) | | 12.5434 | 12.5432 | 12.5429 | 12.5429 | 12.5427 | 12.5425 | 12.5425 | 12.5425 | 12.5425 |
| 6 | U 1 right | cm | 4.585 | 4.585 | 4.590 | 4.580 | 4.590 | 4.735 | 4.735 | 4.735 | 4.730 |
| 7 | U 1 left | do | 5.970 | 5.960 | 5.980 | 5.980 | 5.985 | 6.115 | 6.115 | 6.130 | 6.130 |
| 8 | U 2 R | do | 7.560 | 7.565 | 7.570 | 7.570 | 7.570 | 7.710 | 7.715 | 7.715 | 7.715 |
| 9 | U 2 L | do | 4.440 | 4.440 | 4.440 | 4.435 | 4.440 | 4.575 | 4.585 | 4.585 | 4.585 |
| 10 | U 3 R | do | 7.425 | 7.430 | 7.430 | 7.425 | 7.430 | 7.600 | 7.600 | 7.600 | 7.600 |
| 11 | U 3 L | do | 6.725 | 6.725 | 6.730 | 6.730 | 6.725 | 6.870 | 6.865 | 6.875 | 6.870 |
| 12 | U 4 R | do | 6.390 | 6.395 | 6.410 | 6.400 | 6.405 | 6.550 | 6.555 | 6.550 | 6.555 |
| 13 | U 4 L | do | 7.595 | 7.590 | 7.600 | 7.595 | 7.595 | 7.740 | 7.740 | 7.740 | 7.746 |
| 14 | U 5 R | do | 275.635 | 275.635 | 275.660 | 275.645 | 275.640 | 275.835 | 275.840 | 275.835 | 275.835 |
| 15 | Tape correction | do | .065 | .067 | .100 | .100 | .100 | .102 | .102 | .102 | .103 |
| 16 | Compressibility correction +.007; air column −0.201 | cm | −.014 | −.014 | −.014 | −.014 | −.014 | −.014 | −.014 | −.014 | −.014 |
| 17 | Distance between zeros | do | 937.060 | 937.060 | 937.060 | 937.060 | 937.060 | 937.060 | 937.060 | 937.060 | 937.060 |
| 18 | Subtotal | do | 1,263.466 | 1,263.488 | 1,263.506 | 1,263.506 | 1,263.526 | 1,264.878 | 1,264.898 | 1,264.913 | 1,264.914 |
| 19 | U 5 L | do | −31.705 | −31.705 | −31.690 | −31.690 | −31.695 | −31.500 | −31.500 | −31.500 | −31.500 |
| 20 | (Hg minus $H_2O$) | do | 1,231.771 | 1,231.783 | 1,231.806 | 1,231.816 | 1,231.831 | 1,233.378 | 1,233.398 | 1,233.413 | 1,233.414 |
| 21 | Water | do | 226.8 | 226.8 | 226.8 | 226.8 | 226.8 | 227.1 | 227.1 | 227.1 | 227.1 |
| 22 | Oil | do | −12.6 | −12.6 | −12.6 | −12.6 | −12.6 | −12.6 | −12.5 | −12.5 | −12.5 |
| 23 | Density×cm (Hg minus $H_2O$) | gram weight/cm² | 15,450.6 | 15,450.5 | 15,451.2 | 15,450.5 | 15,450.5 | 15,469.6 | 15,469.9 | 15,470.1 | 15,470.1 |
| 24 | Water | do | 226.3 | 226.3 | 226.3 | 226.3 | 226.3 | 226.6 | 226.6 | 226.6 | 226.6 |
| 25 | Oil | do | −11.2 | −11.2 | −11.2 | −11.2 | −11.2 | −11.2 | −11.1 | −11.1 | −11.1 |
| 26 | A (fig. 2) | do | 15,665.7 | 15,665.6 | 15,666.3 | 15,665.6 | 15,665.6 | 15,685.0 | 15,685.4 | 15,685.6 | 15,685.6 |
| 27 | Time | | 12.20 | 1.30 | 1.47 | 2 | 2.35 | 2.55 | 3.25 | 3.50 | 4.10 |

In this table, each column represents a separate measurement of pressure, which was made simultaneously with a measurement of the same pressure recorded in the corresponding column of Table 4. Such symbols as U 2 R indicate the meniscus of which the associated numbers are the scale readings; U 2 indicates the particular U tube (fig. 2), and the letter R (or L) the branch of the tube right (or left). Item 16 is the sum of the correction for the compressibility of the mercury, oil, and water and of that for the weight of an air column of a height equal to the vertical distance between $C$ and $A$. (Fig. 2.) Item 17 is the sum of the vertical distances between the zeros of the short scales on each of the first four U tubes. Item 20 is equal to the quantity $H$ of equation (3) increased by $(At_c - At_a)$ expressed in centimeters of a hypothetical liquid of density equal to $(\rho_{Hg} - \rho_w)$. Item 21 is the height of the water column $BC$ (fig. 2, equation (3)), and item (22) is the height of the oil column ($AB$ fig. 2, $h_o$ equation (3)). The tape reading of the oil-water meniscus is recorded in Table 4. When item (26), the sum of items (23), (24), and (25) is multiplied by the value of $g$ at this laboratory and the product is increased by $p_{cap}$, the gage pressure at $A$ (fig. 2) is obtained in dynes per cm$^2$. The value of $p_{cap}$ is exceedingly small if the tubes are tapped before readings are taken. In the present work it has been assumed to be negligible. The other items of the table are self-explanatory.

TABLE 3.—*Record of pressure measurements with the piston gage*

Observer C. H. M. Computed by C. H. M. Gage 4–C–12083, renown engine oil, 6 r. p. m. clockwise. Date Mar. 2, 1928

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Observed temperature °C | 22.7 | 23.4 | 24.0 | 24.0 | 24.0 | 24.0 | 24.0 | 24.2 | 24.2 |
| Corrected temperature do | 21.8 | 22.5 | 23.1 | 23.1 | 23.1 | 23.1 | 23.1 | 23.3 | 23.3 |
| Effective height gage cm | 61.37 | 61.37 | 61.37 | 61.37 | 61.37 | 61.37 | 61.37 | 61.37 | 61.37 |
| Oil-water meniscus do | 48.8 | 48.8 | 48.8 | 48.8 | 48.8 | 48.7 | 48.7 | 48.7 | 48.7 |
| Cap and piston g | 1,234.0 | 1,234.0 | 1,234.0 | 1,234.0 | 1,234.0 | 1,234.0 | 1,234.0 | 1,234.0 | 1,234.0 |
| Weights do | 10,000.0 | 10,000.0 | 10,000.0 | 10,000.0 | 10,000.0 | 10,000.0 | 10,000.0 | 10,000.0 | 10,000.0 |
| | 2,000.0 | 2,000.0 | 2,000.0 | 2,000.0 | 2,000.0 | 2,000.0 | 2,000.0 | 2,000.0 | 2,000.0 |
| | 2,000.0 | 2,000.0 | 2,000.0 | 2,000.0 | 2,000.0 | 2,000.0 | 2,000.0 | 2,000.0 | 2,000.0 |
| | 200.0 | 200.0 | 200.0 | 200.0 | 200.0 | 200.0 | 200.0 | 200.0 | 200.0 |
| | 200.0 | 200.0 | 200.0 | 200.0 | 200.0 | 200.0 | 200.0 | 200.0 | 200.0 |
| | | | | | | 20.0 | 20.0 | 20.0 | 20.0 |
| Sum of weights do | 15,634.0 | 15,634.0 | 15,634.0 | 15,634.0 | 15,634.0 | 15,654.0 | 15,654.0 | 15,654.0 | 15,654.0 |
| Buoyancy correction do | −2.2 | −2.2 | −2.2 | −2.2 | −2.2 | −2.2 | −2.2 | −2.2 | −2.2 |
| Corrected sum do | 15,631.8 | 15,631.8 | 15,631.8 | 15,631.8 | 15,631.8 | 15,651.8 | 15,651.8 | 15,651.8 | 15,651.8 |
| Area at observed temperature $cm^2$ | .99784 | .99784 | .99780 | .99784 | .99784 | .99788 | .99786 | .99785 | .99785 |
| Temperature correction do | −.00004 | −.00006 | −.00007 | −.00007 | −.00007 | −.00007 | −.00007 | −.00007 | −.00007 |
| Area at 20° C do | .99780 | .99778 | .99773 | .99777 | .99777 | .99781 | .99779 | .99778 | .99778 |
| Time | 12.20 | 1.30 | 1.47 | 2 | 2.35 | 2.55 | 3.20 | 3.40 | 4.05 |
| Pressure approaching equilibrium | (+) | (−) | (+) | (1) | (−) | (+) | (−) | (+) | (−) |

[1] Piston not disturbed.

Table 3 is the corresponding record for the piston gage. In this table the items "effective height of gage" and "oil-water meniscus" are, respectively, the elevations in centimeters, of the effective bottom of the piston ($A$, fig. 2) and of the oil-water meniscus ($B$, fig. 2) above the zero of the 2.8 m scale. The several values given for the "area at observed temperature" are obtained by dividing each of the several numbers in the preceding line (corrected sum of the weights) by the corresponding number in item 26 of Table 2; this area is the effective area of the piston at the existing temperature of the gage. In deducing from this the area at 20° C., it was assumed that the coefficient of linear expansion of the piston and cylinder is 0.0000115 per °C. A + in the last line of the table indicates that the piston rose to equilibrium; a − that it descended. The other items are self-explanatory.

In using the piston gage to measure pressure, the absolute pressure at $A$ (fig. 2) is calculated from

$$P_A = At_A + \frac{Wg}{a} \tag{4}$$

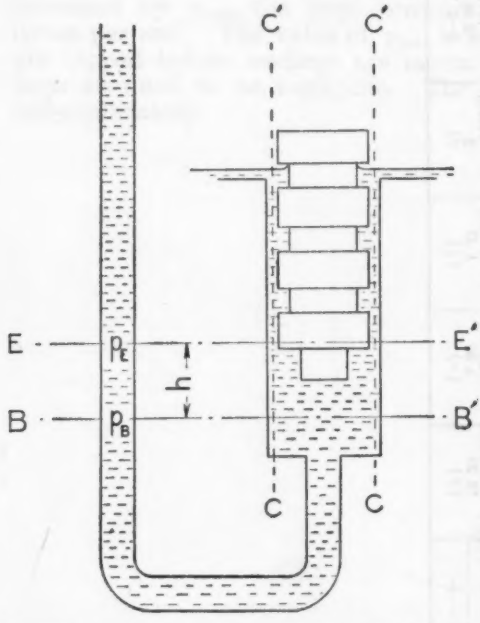


FIGURE 6.—*Diagram showing the effective elevation of an irregular piston*

where $At_A$ is the pressure of the atmosphere at $A$ (fig. 2), $W$ is the sum of the weights, including the weight of the piston, etc., corrected for the buoyancy of the atmosphere, $a$ is the effective area of the piston as determined from the comparison with the manometer, and $g$ is the acceleration due to gravity (980.091 in this laboratory).[5] The pressure at any other point, such as $B$, differs from that at $A$ by an amount depending on the difference in level of $A$ and $B$, and on the density of the fluid or fluids in the connecting tubing.

If there were no leakage of oil past the piston, and if its base were a horizontal plane, then the area $a$ in equation (4) would be the actual cross-sectional area of the piston, and the level of $A$ (fig. 2), at which the pressure is given by equation (4), would be the level of the base of the piston. For convenience in construction, and also for the protection of the lapped surfaces, each of the pistons used in the gages described here has near its base a short section whose diameter is less than that of the main body of the piston. Each piston also has a center hole in its base. Further, there is always some leakage of oil past the piston. It is still possible, however, to use the expression (4) to calculate the pressure at some height, called the effective height of the gage. This may be shown as follows: Figure 6 illustrates

[5] B. S. Bull., 8, p. 363; 1911. (Sci. Paper No. 171).

a gage whose piston, for the sake of generality, has not only the smaller section at the bottom, but also grooves at several places along its length. It is assumed that the grooves are deep enough so that there is no appreciable pressure drop due to the flow of the oil across them. Consider the cylindrical surface of radius $r$, represented by the dotted lines $CC'$ (fig. 6), located where there is no shear in the oil film. The material outside this cylinder does not exert any vertical force on the material inside the cylinder. It follows that the pressure in the oil at any level $B$ is given by

$$P_B = At_B + \frac{Wg + (\rho_o - \rho')\, vg}{\pi r^2}$$

where $v$ is the volume of oil above $B$ and inside the cylinder $CC'$ and $\rho'$ the density of air. The pressure in the connecting tube at any level $E$ at a height $h$ above $B$ is

$$P_E = At_B + \frac{W\,g + (\rho_o - \rho')\, v\, g}{\pi r^2} - \rho_o\, g\, h$$

$$= At_E + \frac{W\,g + (\rho_o - \rho')\, v\, g - \pi r^2\, (\rho_o - \rho')\, g\, h}{\pi r^2}$$

now if $E$ be so chosen that

$$h = \frac{v}{\pi r^2}$$

then the pressure at $E$ is given by

$$P_E = At_E + \frac{W\,g}{\pi r^2}$$

which is of the same form as equation (4). This is equivalent to choosing the level $E$ so that the volume of oil within the cylinder $CC'$ and above $E$ is equal to the volume of that part of the piston which lies below $E$. The area $\pi r^2$ is called the effective area of the gage, and $E$ is called the effective elevation of the piston. If the pressure (measured by the manometer) at any other level were used to compute the effective area by means of the formula

$$a = \frac{W\,g}{P - At}$$

the value found would not be constant, but would be a function of the pressure.

The weights have been calibrated about once every two years; the corrections used were either taken directly from a calibration or from an interpolation between calibrations. The first weights were made of cast iron and nickel plated. These gradually increased in weight, the increase being about 3 g in 10 years for the 20 kg weights and proportionately smaller for the smaller weights. More recently 20 kg nickel-plated steel weights and smaller nickel-plated brass weights were constructed and adjusted to within 0.1 or 0.2 g of the correct value. The changes in these 20 kg weights, with two exceptions, were 0.3 g or less in two years. The smaller nickel-plated brass weights have undergone no appreciable changes.

## VII. CALIBRATION OF PISTON GAGES

The calibration of a piston gage consists essentially in the determination of the effective area of the piston. This may be accomplished in two ways, namely: (1) The gage may be calibrated as a secondary gage by comparison with a mercury manometer, and (2) the gage may be calibrated as a primary instrument by measurement of various dimensions of the gage.

### 1. CALIBRATION AS A SECONDARY INSTRUMENT BY COMPARISON WITH A MANOMETER

The results of comparisons up to 15 bars, of individual piston gages with the manometer are presented in Table 4, the table being arranged so that the measurements with each gage form a group. The notation used to represent the gages is indicated in Table 1.

TABLE 4.—*Comparison of individual piston gages with the manometer*

| Date | Number of observations | Pressure (gage) | Effective area at 20° C. | Effective diameter at 20° C. | Average deviation from mean area | Remarks |
|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| | | | MEASUREMENTS WITH GAGE 1-A | | | |
| | | *Bars* | *cm²* | *cm* | *cm²* | |
| June, 1918 | 20 | 9.2–15.3 | 1.00294 | 1.13004 | 0.00022 | |
| May, 1919 | 66 | 4.0–14.6 | 1.00311 | 1.13013 | .00019 | |
| November, 1919 | 44 | 15.1 | 1.00269 | 1.12990 | .00010 | |
| July, 1924 | 22 | 15.4 | 1.00266 | 1.12988 | .00003 | |
| August, 1925 | 16 | 15.3 | 1.00268 | 1.12989 | .00005 | |
| | | | MEASUREMENTS WITH GAGE 2-A | | | |
| Mar. 25, 1926 | 8 | 15.2 | 1.00649 | 1.13203 | 0.00005 | Base 30213. |
| Mar. 27, 1926 | 5 | 15.2 | 1.00652 | 1.13205 | .00004 | Base 30213. |
| Apr. 12, 1926 | | | | | | Lapped piston, change in weight indicates a decrease of 0.00006 cm. in piston diameter. |
| May 12, 1926 | 10 | 15.0 | 1.00650 | 1.13204 | .00006 | Base 12083. |
| May 14, 1926 | 7 | 15.2 | 1.00654 | 1.13206 | .00005 | Base 12083. |
| May 26, 1926 | | | | | | Lapped piston, change in weight indicates a decrease of 0.00001 cm. in piston diameter. |
| June 2, 1926 | 10 | 15.3 | 1.00650 | 1.13204 | .00003 | Base 12083. |
| June 25, 1926 | 4 | 15.3 | 1.00645 | 1.13201 | .00002 | Base 30213. |
| June 28, 1926 | 3 | 15.3 | 1.00650 | 1.13204 | .00004 | |
| June 29, 1926 | 4 | 15.3 | 1.00651 | 1.13205 | .00001 | Base 30213, motor removed 25 cm. |
| July 1, 1926 | 4 | 15.3 | 1.00654 | 1.13206 | .00002 | |
| Do | 4 | 15.3 | 1.00648 | 1.13203 | .00002 | Base 30213, motor replaced. |
| Aug. 4, 1927 | 5 | 15.4 | 1.00643 | 1.13200 | .00003 | Base 12083. |
| Aug. 6, 1927 | 8 | 15.3 | 1.00641 | 1.13199 | .00002 | Base 12083. |
| | | | MEASUREMENTS WITH GAGE 3-B | | | |
| Aug. 11 and 12, 1925 | 16 | 15.3 | 0.99632 | 1.12630 | 0.00008 | Base 30213. |
| Mar. 16, 1926 | 12 | 15.3 | .99629 | 1.12628 | .00003 | Base 30213. |
| Mar. 13, 1928 | 4 | 15.4 | .99612 | 1.12619 | .00001 | Base 12083. |
| May 16, 1928 | 4 | 15.2 | .99610 | 1.12618 | .00001 | Base 12083. |
| | | | MEASUREMENTS WITH GAGE 3-C | | | |
| June 2, 8, and 10, 1927 | 25 | 15.2 | 0.99676 | 1.12655 | 0.00003 | Base 30213. |

TABLE 4.—*Comparison of individual piston gages with the manometer*—Continued

MEASUREMENTS WITH GAGE 4-C

| Date | Number of observations | Pressure (gage) | Effective area at 20° C. | Effective diameter at 20° C. | Average deviation from mean area | Remarks |
|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| | | *Bars* | *cm²* | *cm* | *cm²* | |
| Mar. 9, 1926 | 9 | 15.4 | 0.9972 | 1.1267 | 0.002 | Piston sticking badly, lapped September, 1927. |
| Mar. 2, 1928 | 9 | 15.4 | .99777 | 1.12712 | .00001 | Base 12083. |

MEASUREMENTS WITH 10-BAR GAGE

| | | | | | | |
|---|---|---|---|---|---|---|
| Dec. 11 and 12, 1925 | 19 | 3.1 | 9.9977 | 3.5679 | 0.0004 | Base 30778. |
| Dec. 16 and 17, 1925 | 20 | 6.2 | 9.9981 | 3.5679 | .0003 | |
| Dec. 21 and 23, 1925 | 16 | 9.3 | 9.9982 | 3.5679 | .0004 | |
| May 23, 1928 | 10 | 9.1 | 9.9976 | 3.5678 | .0002 | |

For pressures higher than about 15 bars, a method described by Holborn and Schultze was used.[6] In this method two piston gages were connected to the manometer, one to the high-pressure end, the other to the low-pressure end. Observations were made with the first of these piston gages balanced against the combined pressure exerted by the manometer and the second piston gage, the manometer being adjusted to exert a pressure of approximately 15 bars and the second piston gage adjusted to exert its minimum pressure of 1.5 bars. The load on each gage was then increased by steps of 15 kg and the observations repeated at each pressure until the maximum pressure of 75 bars was reached. This procedure was then repeated with the two piston gages interchanged. The bases were not interchanged. The observations thus obtained provided data for calculating the effective areas of both gages at pressures up to 75 bars, the limit set by the strength of the glass in the manomter. The results of these comparisons are given in Table 5 where the gage connected to the low-pressure end of the manometer is referred to as the first piston gage, and that connected to the high-pressure end as the second gage. The value used in column 4 for the effective area at both 1.5 and 16.3 bars was the mean of values taken from column 8 and from Table 4 for the same gage at approximately 15 bars. The effective areas of both gages at about 32 bars, given in column 8, were calculated from these data and then used for calculation with observations at the next higher pressure.

[6] Ann. Physik. (ser. 4), **47**, p. 1089; 1915.

TABLE 5.—*Comparison between two piston gages and the manometer*

| Date | Number of observations | First piston gage | | | Second piston gage | | | |
|---|---|---|---|---|---|---|---|---|
| | | Gage No. | Effective area at 20° C. | Pressure (gage) | Gage No. | Pressure (gage) | Calculated effective area, 20° C. | Average deviation from mean |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| | | | *cm²* | *Bars* | | *Bars* | *cm²* | *cm²* |
| Apr. 13, 1928 | 5 | 4-C-30213 | 0.99776 | 1.5 | 3-B-12083 | 16.7 | 0.99606 | 0.00006 |
| Apr. 14, 1928 | 2 | 4-C-30213 | .99776 | 1.5 | 3-B-12083 | 16.7 | .99609 | 0 |
| Apr. 16, 1928 | 2 | 4-C-30213 | .99776 | 1.5 | 3-B-12083 | 16.7 | .99608 | .00003 |
| Apr. 17, 1928 | 2 | 4-C-30213 | .99776 | 1.5 | 3-B-12083 | 16.7 | .99606 | .00003 |
| Apr. 18, 1928 | 5 | 4-C-30213 | .99776 | 16.3 | 3-B-12083 | 31.4 | .99608 | .00005 |
| Apr. 19, 1928 | 5 | 4-C-30213 | .99773 | 30.0 | 3-B-12083 | 45.0 | .99606 | .00004 |
| | 5 | 4-C-30212 | .99773 | 45.8 | 3-B-12083 | 60.8 | .99605 | .00003 |
| Apr. 27, 1928 | 5 | 3-B-30213 | .99608 | 1.5 | 4-C-12083 | 16.5 | .99778 | .00005 |
| Apr. 28, 1928 | 6 | 3-B-30213 | .99608 | 1.5 | 4-C-12083 | 16.5 | .99773 | .00002 |
| | 2 | 3-B-30213 | .99608 | 16.3 | 4-C-12083 | 31.2 | .99773 | .00001 |
| Apr. 30, 1928 | 4 | 3-B-30213 | .99608 | 16.3 | 4-C-12083 | 31.3 | .99773 | .00001 |
| | 4 | 3-B-30213 | .99608 | 31.1 | 4-C-12083 | 46.0 | .99773 | .00001 |
| May 2, 1928 | 6 | 3-B-30213 | .99606 | 45.8 | 4-C-12083 | 60.7 | .99771 | .00002 |
| May 3, 1928 | 1 | 3-B-30213 | .99606 | 60.6 | 4-C-12083 | 75.4 | .99771 | |
| May 4, 1928 | 3 | 3-B-30213 | .99606 | 60.6 | 4-C-12083 | 75.4 | .99771 | .00001 |
| May 7, 1928 | 4 | 4-C-30213 | .99771 | 60.5 | 3-B-12083 | 75.5 | .99605 | .00004 |
| May 8, 1928 | 4 | 4-C-30213 | .99776 | 1.5 | 3-B-12083 | 16.4 | .99609 | .00002 |
| May 10, 1928 | 4 | 4-C-30213 | .99776 | 1.5 | 3-B-12083 | 16.5 | .99610 | .00003 |
| May 11, 1928 | 4 | 4-C-30213 | .99776 | 1.5 | 3-B-12083 | 16.5 | .99608 | .00002 |

The precision obtained for the comparisons at the high pressures was about the same as at 15 bars; that is, a few parts in 100,000.

Table 6 presents the results of direct comparisons of piston gages, and provides a check on some of the data in the two preceding tables. The contents of the first six columns need no explanation. The observed ratio of the areas of the two gages corrected to the same temperature is given in column 7. The same ratio calculated from data in the preceding tables is given in column 8, and the number of the table from which the data were taken is given in column 9. In the last five observations the speed of rotation of the pistons was purposely varied over a wide range in order to ascertain whether the effective areas of the gages were altered by changing the speed of rotation, as is suggested by the work of Wagner.[7] No such effect is indicated.

[7] Wagner, Ann. Physik. (ser. 4), **15**, p. 906; 1904.

TABLE 6.—*Comparison of piston gages*

| Date | First gage | | Second gage | | Pressure (gage) | Observed ratio of areas 1st/2d | Calculated ratio | Source of calculated ratio |
|---|---|---|---|---|---|---|---|---|
| | No. | Revolutions per minute | No. | Revolutions per minute | | | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| | | | | | *B* | | | *Table No.* |
| Mar. 31, 1926 | 2-A-30213 | | 10 bar | | 9.06 | 0.100660 | | |
| 1925 to 1926 | 2-A | | 10 bar | | 9.06 | | 0.100670 | 4 |
| Mar. 7, 1928 | 3-B-30213 | 18cc | 4-C-12083 | 6c | 21.2 | .99832 | | |
| Mar. 9, 1928 | 3-B-30213 | 18cc | 4-C-12083 | 6c | 21.2 | .99838 | | |
| Mar. 10, 1928 | 3-B-30213 | 18cc | 4-C-12083 | 6c | 21.2 | .99836 | | |
| March, 1928 | 3-B | | 4-C | | 21.2 | | .99833 | 5 |
| Mar. 12, 1928 | 3-B-30213 | 10cc | 4-C-12083 | 4c | 40.8 | .99835 | | |
| | 3-B-30213 | 10cc | 4-C-12083 | 4c | 40.8 | .99837 | | |
| March, 1928 | 3-B | | 4-C | | 40.8 | | .99833 | 5 |
| Mar. 12, 1928 | 3-B-30213 | 10cc | 4-C-12083 | 4c | 60.4 | .99836 | | |
| | 3-B-30213 | 10cc | 4-C-12083 | 4c | 60.4 | .99834 | | |
| March, 1928 | 3-B | | 4-C | | 60.4 | | .99833 | 5 |
| Mar. 13, 1928 | 3-B-30213 | 10cc | 4-C-12083 | 4c | 80.1 | .99835 | | |
| | 3-B-30213 | 10cc | 4-C-12083 | 4c | 80.1 | .99835 | | |
| March, 1928 | 3-B | | 4-C | | 80.1 | | .99833 | 5 |
| May 25, 1928 | 4-C-30213 | 7cc | 10 bar | 5.5c | 9.04 | .099807 | | |
| | 4-C-30213 | 7cc | 10 bar | 5.5c | 9.04 | .099799 | | |
| | 4-C-30213 | 7cc | 10 bar | 5.5c | 9.09 | .099806 | | |
| | 4-C-30213 | 7cc | 10 bar | 5.5c | 9.09 | .099797 | | |
| | 4-C-30213 | 7cc | 10 bar | 5.5c | 9.11 | .099797 | | |
| | 4-C-30213 | 7cc | 10 bar | 5.5c | 9.11 | .099806 | | |
| | 4-C-30213 | 7cc | 10 bar | 5.5c | 9.12 | .099799 | | |
| | 4-C-30213 | 7cc | 10 bar | 5.5c | 9.12 | .099807 | | |
| May, 1928 | | | | | | | .099801 | 4 |
| Jan. 4, 1929 [1] | 4-C-12083 | 8c | 10 bar | 2.4cc | 8.17 | .099799 | | |
| | 4-C-12083 | 4c | 10 bar | 6.2cc | 8.17 | .099800 | | |
| | 4-C-12083 | 3.2c | 10 bar | 2.9cc | 8.17 | .099801 | | |
| | 4-C-12083 | 4c | 10 bar | 4.1cc | 8.17 | .099800 | | |
| | 4-C-12083 | 18c | 10 bar | 4.1cc | 8.17 | .099800 | | |

NOTE.—"c" represents clockwise rotation, "cc" represents counterclockwise.

[1] All observations given for this date were made with piston 4-C-12083 moving upward toward equilibrium.

Some authors have stated a preference for oscillatory rotation of the piston, instead of continuous rotation, and have claimed that the former method maintains the piston more nearly in a central position in the cylinder.[8]

For gages with pistons sticking at a definite azimuth, the use of oscillatory rotation enables the observer to adjust the piston to such azimuth as to reduce sticking to a minimum. In the present investigation the torque required for rotating the pistons at speeds of four or more revolutions per minute was proportional to the speed, a condition indicating that there was a complete film of oil around the piston, and that the latter was fairly well centered. A comparison of the results obtained in this investigation with those published in the various papers referred to in the Appendix shows that equally precise pressure measurements have been made with both types of gages.

In one instance [9] it has been reported that the effective area of piston gages changed with the pressure by as much as 2 parts in 1,000

[8] F. G. Keyes and Jane Dewey, J. Opt. Soc. of Am. **14**, p. 491; 1927.
[9] Crommelin and Smid, Leiden Comm. No. 146c; 1915.

for pressures up to 100 bars, but calculation of the strains caused by pressures in that range indicate that there should be no such large change in any gage having metal parts of reasonable thickness. The data of the present investigation show no appreciable changes of this nature up to the highest pressure observed, 75 bars. The slight variations which do appear in the table are no greater than the experimental error.

## 2. CALIBRATION AS A PRIMARY INSTRUMENT, BY MEASUREMENT OF VARIOUS DIMENSIONS

Considerable effort was devoted to the calibration of the piston gages as primary, or absolute instruments. As stated in the preceding section, only when there is no leakage of oil past the piston is the area used for calculating the pressure the same as the cross-sectional area of the piston. Such a condition is not practicable, since its attainment requires a piston and cylinder in the form of true geometric cylinders of revolution having the same diameter. In actual gages the true geometric form is approximated as nearly as possible and the cylinder made slightly larger than the piston, the choice of sizes being a compromise in which the difference must be large enough to prevent the sticking caused by deviations from true form and yet small enough to avoid excessive leakage of fluid past the piston. In such gages the effective area is an average of the cross-sectional area of a surface lying somewhere between the surfaces of the piston and cylinder. The process of lapping is likely to leave the piston small at the ends, although in these gages this irregularity extends only over a short distance as illustrated for piston No. 1 in Figure 7. Similarly, the ends of the cylinders are likely to be large. These irregularities cause a tapering crevice. Secular changes in the steel may cause the piston or cylinder to become elliptical or the axis of either to become curved. Even though pistons and cylinders of true geometric form are attained, the slightest eccentricity in the application of the load will result in a torque which will throw the axis of the piston out of parallel with that of the cylinder.

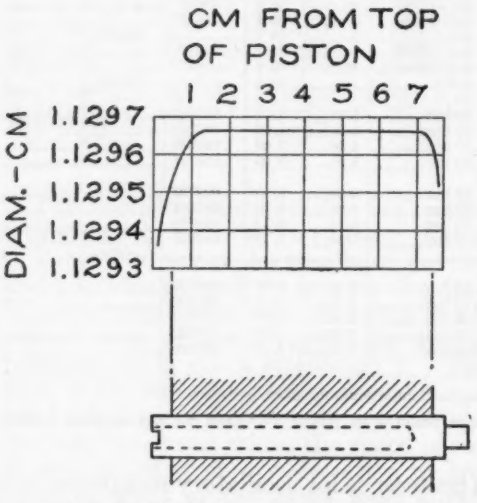


FIGURE 7.—*Contour of piston No. 1*

These possible causes of irregularity are so numerous that a combination of circumferential and axial variations in the width of crevice is to be expected. An approximate determination of the effective area can be made from a measurement of the average diameters of the piston and cylinder or from a measurement of the average piston diameter and the width of crevice between the piston and cylinder.

Wagner [10] determined the average diameter of gage cylinders from their length and the amount of mercury required to fill them. This method was not used in the present investigation, since it appeared that a measurement of crevice width offered equally accurate results, with less experimental difficulty. Three experimental methods were used for determining the width of crevice, the first involving a measurement of the oil leakage past the piston, the other two involving the use of the gage as a torsional viscometer. Before entering into experimental details and presenting the observed data, the fundamental relations between the dimensions of the piston and cylinder, and the sizes of the observed quantities will be discussed in the following order: (1) A formula for calculating the effective radius will be developed. The effective width of crevice—that is, the amount to be added to the diameter of the piston to obtain the diameter corresponding to the effective area—will be shown to differ by a negligible amount from the difference between the radii of the piston and cylinder, which are assumed to be coaxial cylinders of revolution; (2) formulas for calculating the difference between the radii of the piston and cylinder from data obtained by using the gage as a viscometer will be developed, the assumptions in regard to the piston and cylinder being the same as before; (3) a discussion will be given of the errors involved in the application of these formulas to a gage in which the crevice tapers along the axis but is uniform at any given cross section; (4) a similar discussion will be given for a gage in which the crevice is uniform along an element of the piston, but varies around a given cross section; and (5) the upward frictional force caused by the gradual descent of the piston in displacing the oil leakage will be discussed.

In these discussions the following notation will be used:

$\mu$ = the viscosity, in poises, of the fluid used in the gage.
$Q$ = rate of leakage of fluid, in cm$^3$ per second.
$v$ = velocity at any given point, in cm per second.
$L$ = length of crevice, in cm.
$r_1$ = radius of piston, in cm.
$r_2$ = radius of cylinder, in cm.
$r_m = \frac{r_1 + r_2}{2}$.
$R$ = effective radius, in cm.
$p$ = excess, over the atmospheric pressure, of the pressure acting upward at the base of the piston (dynes per cm$^2$).
$f$ = load on gage, in dynes.
$T$ = torque, in dyne cm.
$\omega$ = angular velocity, in radians per second.
$n$ = speed of rotation, in revolutions per second.
$I$ = moment of inertia of rotating system (g cm$^2$).
$t$ = time, in seconds.

1. The effective radius may be calculated as follows: Consider a hypothetical cylinder coaxial with the piston and steel cylinder, which may have a radius $r$ anywhere between the limits $r_1$ and $r_2$. The forces acting on this cylinder will be the downward force $f$ due to the load, the upward force $p\pi r^2$ due to the pressure, and the force due

[10] Ann. Physik. (ser. 4), **15**, p. 906; 1904.

to the viscous drag of the oil which is $2\pi rL\mu\frac{dv}{dr}$, streamline flow being assumed. For equilibrium conditions the sum of these forces is equal to zero; that is

$$f-p\pi r^2-2\pi rL\mu\frac{dv}{dr}=0 \tag{5}$$

Integration of the above equation gives

$$f\log_e r-\frac{p\pi r^2}{2}-2\pi L\mu v=C \tag{6}$$

where $C$ is a constant of integration.

Since the velocity of the fluid must be zero at the surface of the piston and of the cylinder, $v=0$ for $r=r_1$ and $r=r_2$.

Substitution of these limiting conditions in equation (6) gives

$$C=\frac{p\pi\ (r_2^2\log_e r_1-r_1^2\log_e r_2)}{2\log_e\frac{r_2}{r_1}} \tag{7}$$

and

$$f=\frac{p\pi\ (r_2^2-r_1^2)}{2\log_e\frac{r_2}{r_1}} \tag{8}$$

Since the effective area is defined as the load divided by the pressure, the effective radius deduced from equation (8) is

$$R=\sqrt{\frac{f}{p\pi}}=\sqrt{\frac{r_2^2-r_1^2}{2\log_e\frac{r_2}{r_1}}} \tag{9}$$

The only assumptions made in deducing this value for the effective radius are that the piston is a true geometric cylinder of circular cross section inside of and coaxial with a hollow cylinder of similar form, and that the flow is stream line. The latter assumption is justified by the fact that the velocity is much smaller than that which Buckingham[11] has shown to be necessary for the production of turbulence.

For comparison with the values of effective radius used by some other authors, that deduced here may be converted into another form by substituting

$$\frac{r_2}{r_1}=1+x$$

and the formula

$$\log\ (1+x)=x-\frac{x^2}{2}+\frac{x^3}{3}-\frac{x^4}{4}\cdots\cdots$$

in equation (9).

[11] Engineering, **115**, p. 225; 1923.

The cube term in the series obtained is zero and the higher powers are quite negligible.

Whence

$$R=\sqrt{r_2 r_1+\frac{(r_2-r_1)^2}{6}-\ldots.} \tag{9a}$$

Klein [12] has considered the effective area to be the mean of the areas of the piston and cylinder. The effective radius thus defined is

$$R'=\sqrt{\frac{r_2^2+r_1^2}{2}}=\sqrt{r_2 r_1+\frac{(r_2-r_1)^2}{2}} \tag{10}$$

Some authors have used the mean of $r_2$ and $r_1$; that is,

$$R''=\frac{r_2+r_1}{2}=\sqrt{r_2 r_1+\frac{(r_2-r_1)^2}{4}} \tag{11}$$

Since in piston gages the difference between $r_2$ and $r_1$ is less than one-thousandth part of these radii, it is easily seen that the three values of $R$ defined by equations (9) or (9a), (10), and (11) will differ by less than 1 part in 1,000,000. The value derived in this paper (equation (9)), which is exactly correct for the conditions assumed, is smaller than either of the other two values, but all three are so nearly equal that the difference is only of academic interest.

If the effective width of crevice $W_1$ is defined as the amount to be added to the piston diameter to obtain the diameter corresponding to the effective area, then

$$W_1=2\ (R-r_1)=2\left[\sqrt{\frac{r_2^2-r_1^2}{2\log_e\frac{r_2}{r_1}}}-r_1\right] \tag{12}$$

From the preceding discussion in regard to $R$, it is easily deduced that the effective width $W_1$ is negligibly smaller than the true width $(r_2-r_1)=W$.

2a. The difference between the radii of the piston and cylinder may be calculated from the rate of leakage past the piston, by substitution of equations (6), (7), and (8) in the equation

$$Q=\int_{r_1}^{r_2} v 2\pi r\, dr$$

and performing the integration. After several algebraic transformations one obtains

$$Q=\frac{\pi p r_1^4}{8\ L\mu}\left[\left(\frac{r_2^4}{r_1^4}-1\right)-\frac{\left(\frac{r_2^2}{r_1^2}-1\right)^2}{\log_e\frac{r_2}{r_1}}\right] \tag{13}$$

This equation is also derived in H. Lamb's Hydrodynamics, fifth edition, page 555.

[12] Berlin T. H. Diss., 1909. George Klein, Untersuchung und Kritik von Hochdruckmessern.

By following the same procedure as used in reducing equation (9) to the form (9a), equation (13) may be converted into the form

$$Q=\frac{\pi p r_1^4}{8L\mu}\left[\frac{4}{3}x^3+\frac{2}{3}x^4+\frac{x^5}{45}+\cdots\cdots\right]$$

where, as before

$$x=\frac{r_2}{r_1}-1=\frac{W}{r_1}$$

or

$$Q=\frac{p\pi r_1(r_2-r_1)^3}{6L\mu}\left[1+\frac{W}{2r_1}+\frac{\left(\frac{W}{r_1}\right)^2}{60}+\cdots\right] \tag{14}$$

Since this equation is to be used in calculating $(r_2-r_1)$, a quantity which enters as a small correction to the piston diameter, and since for piston gages in general, $\frac{W}{r_1}$ has a value less than 0.001, all terms of the series except the first may be neglected. Whence, denoting the difference in radii calculated in this manner by $W_2$, we obtain equation (15) which was used for calculating the width of crevice from the observed rate of oil leakage past the piston.

$$W_2=r_2-r_1=\sqrt[3]{\frac{6L\mu Q}{p\pi r_1}} \tag{15}$$

The terms that were found to be negligible in the series of equation (14) correct for the curvature of the crevice, and equation (15) represents exactly the relation between the width of crevice between two infinite plane surfaces and the leakage through a portion of this crevice $2\pi r_1$ in width.

2b. The width of crevice may be calculated from measurements of the torque required to rotate the piston, as follows:

The torque is represented by the equation

$$T=-2\pi r^3 L\mu\frac{d\omega}{dr}$$

where $\omega$ is the angular velocity in the lubricant at the radius $r$. Whence

$$\int_{r_1}^{r_1}\frac{dr}{r^3}=-\int_0^{\omega_1}\frac{2\pi L\mu d\omega}{T}$$

$\omega_1$ being the angular velocity of the piston. Integrating and substituting $2\pi n$ for $\omega_1$ gives

$$\frac{4\pi^2 L\mu n}{T}=(r_2-r_1)\frac{(r_2+r_1)}{2\,r_1^2 r_2^2} \tag{16}$$

If we represent the width of crevice thus calculated by $W_3$ then,

$$W_3=r_2-r_1=\frac{4\pi^2 L\mu n r_m^3}{T}\left(1-\frac{W^2}{2r_m^2}+\frac{W^4}{16r_m^4}\right)$$

The last two terms of the polynomial are negligible, whence

$$W_3=\frac{4\pi^2 L\mu n r_m^3}{T}$$

For the small widths of crevice occurring in piston gages it is amply accurate to substitute in this equation $r_1$ in place of $r_m$ whence

$$W_3=\frac{4\pi^2 L\mu n r_1^3}{T} \tag{17}$$

which is the form used in this investigation for calculating crevice widths from torque measurements at constant speed.

2c. It was found that for constant speeds above a certain minimum the torque measured was proportional to the speed. If this is assumed to be true also for variable speeds then, when the piston and weights are kept rotating only by the inertia of the system, the torque exerted on the cylinder by the piston is

$$T=a\omega=-I\frac{d\omega}{dt} \tag{18}$$

where $a$ is a constant, $I$ is the moment of inertia of the rotating system, and $\omega$ is its angular velocity at any time $t$. Integration of equation (18) gives

$$\omega=\frac{d\theta}{dt}=\omega_1 e^{-\frac{a}{I}(t_2-t_1)}$$

where $\omega_1$ is the angular velocity at the time $t_1$ and $\theta$ is the angular position or azimuth of the rotating system at any time $t$. A second integration gives

$$\theta_2-\theta_1=-\frac{I\omega_1}{a}\left\{e^{-\frac{a}{I}(t_2-t_1)}-1\right\} \tag{19}$$

The determination of $\theta_1$, $\theta_2$, and $\theta_3$ corresponding to the times $t_1$, $t_2$, $t_3$ chosen such that $t_3-t_2=t_2-t_1$ makes it possible to express $a$ as an explicit function of the variables, thus

$$a=\frac{I}{t_2-t_1}\log_e\frac{\theta_3-\theta_2}{\theta_2-\theta_1} \tag{20}$$

But equations (17) and (18) lead to

$$a=\frac{2\pi\ L\ \mu r_1^3}{W_3}$$

Therefore

$$W_3=\frac{2\pi\ L\ \mu r_1^3\ (t_2-t_1)}{I\log_e\frac{\theta_3-\theta_2}{\theta_2-\theta_1}} \tag{21}$$

which is the equation used to calculate the width of crevice from observations of time and corresponding angular position of the rotating system spinning free of any driving mechanism.

The preceding formulas were derived for a crevice of uniform width, but, as already stated, a combination of axial and circumferential

variations in the width of crevice is to be expected. For simplicity, each of the two types of irregularity will be considered separately, and the consequent errors involved in the application of the preceding formulas will be estimated.

3. Errors involved in the application of the formulas to a gage in which the crevice tapers along the axis. For simplicity, it is assumed that the piston is a geometrical cylinder of circular cross section and that the steel cylinder forms a conical frustrum of circular cross section as illustrated in Figure 8. The same notation will be used as

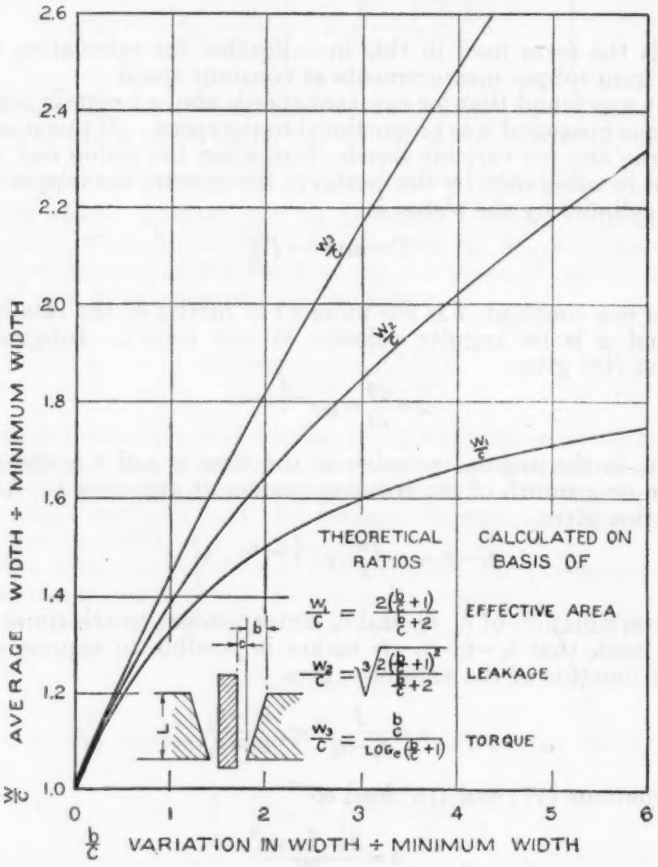


FIGURE 8.—*Effect of taper on the width of crevice as calculated by various methods*

before, and, in addition, $x$ will represent the width of crevice at any distance $y$ from the narrow end of the cylinder. Then

$$x=\frac{by}{L}+c \tag{22}$$

where $c$ is the width of crevice at the narrowest place (see fig. 8), and $b$ is the change in width of crevice from the narrowest to the widest part.

For the sake of convenience, the order in which the formulas were discussed in the preceding section will be changed, and the leakage for the piston and cylinder just described will be calculated first.

From equations (15) and (22) we have for any infinitesimal length of the piston

$$\left\{\frac{by}{L}+c\right\}^3=-\frac{6\ \mu Q}{\pi r_1}\frac{dy}{dp} \tag{23}$$

Integration gives

$$p=\frac{6\ \mu Q}{\pi r_1}\int_{y=0}^{y=L}\frac{dy}{\left\{\frac{by}{L}+c\right\}^3}=\frac{3\ \mu Q\ L}{\pi b\ r_1}\left\{\frac{1}{c^2}-\frac{1}{(b+c)^2}\right\} \tag{24}$$

If, as was done in this investigation, equation (15) is used to calculate $W_2$ then

$$p=\frac{6\ \mu Q\ L}{W_2^3\ \pi r_1}$$

Substitution of this value of $p$ in equation (24) gives

$$\frac{W_2}{c}=\sqrt[3]{\frac{2\ (b/c+1)^2}{b/c+2}} \tag{25}$$

which is the relation between the average width of crevice $W_2$, calculated from the measurement of oil leakage, and the actual dimensions of the crevice.

To deduce the relation between the average effective width and the dimensions shown in Figure 8 it will be assumed that the effective area for each element of length $dy$ is the mean of the corresponding areas of the piston and cylinder. Then the element of force due to the drop in pressure along the element $dy$ is

$$dF=\pi r_1^2\frac{dp}{dy}dy-\pi r_m x\frac{dp}{dy}dy \tag{26}$$

By replacing $r_m$ with the approximate value $r_1$, and by substituting in (26) the value of $\frac{dp}{dy}$ given by equation (23) and the value of $Q$ given by equation (24) we obtain

$$F=\pi r_1^2 p+2\pi p r_1\int_{y=0}^{y=L}\frac{1}{\frac{1}{c^2}-\frac{1}{(b+c)^2}}\frac{b}{Lx^2}dy$$

therefore

$$F=\pi r_1^2 p+2\pi p r_1\left\{\frac{1}{\frac{1}{c}+\frac{1}{(b+c)}}\right\}$$

The effective area of the gage minus the area of the piston is

$$\frac{F}{p}-\pi r_1^2=\frac{2\pi r_1}{\frac{1}{c}+\frac{1}{b+c}}=S$$

The effective width of the crevice, or the amount to be added to the piston diameter for calculating the effective area, is then approximately

$$W_1=\frac{2S}{2\pi r_1}=\frac{2}{\frac{1}{c}+\frac{1}{b+c}}$$

or

$$\frac{W_1}{c}=\frac{2(b/c+1)}{b/c+2} \tag{27}$$

The relation between the average width, calculated from torque measurements and the dimensions $b$ and $c$, is deduced by a method similar to that used for the average width calculated from leakage measurements.

The torque contributed by the element of length $dy$ is (from equation (17))

$$dT=\frac{4\pi^2 r_1^3 n\mu dy}{\frac{by}{L}+c}$$

Integration of this differential equation and substitution in equation (17) gives

$$\frac{W_3}{c}=\frac{b/c}{\log_e\left\{\frac{b}{c}+1\right\}} \tag{28}$$

Values of the three ratios just derived have been calculated for various values of $\frac{b}{c}$ and the data presented graphically in Figure 8. This figure shows that for a tapering crevice the measurement of the actual effective area and piston diameter should give the smallest width, the measurement of leakage a larger value, and the measurement of the torque the largest value of the three.

4. The effect of departures of either piston or cylinder from true circular form may be illustrated by assuming a piston which forms a true cylinder of revolution surrounded by a composite cylinder made up of two or more coaxial segments having different radii. Application of equations (12), (15), and (17) to a specific problem shows that when such irregularities occur, measurement of effective area and piston diameter should give an intermediate value, the measurement of leakage a larger value, while the torque should give the smallest value for the width of crevice.

For a given sectional area, irregularities in the form of piston or cylinder cause less change in the effective width than in the widths determined from oil leakage and torque measurements. In fact, the effective width is essentially unchanged by such irregularities if the dimensions are such as occur in precise piston gages. Michels [13] reached the same conclusion. The equation for the leakage of a

[13] Ann. d. Phys. (ser. 4), **73**, p. 603; 1924.

viscous fluid between a piston and cylinder which are geometric cylinders of revolution and have parallel axes, is

$$Q=\frac{p\pi r_m W_1^3}{6\mu L}\left(1+\frac{3e^2}{2W_1^2}\right)$$

where $e$ is the distance between the axes. This equation, which was derived by Becker,[14] also shows that the leakage is increased by circumferential irregularities.

5. In the paper just referred to, Michels discussed the upward frictional force caused by the gradual sinking of the piston as it displaces the oil which leaks from the gage, and expressed this force in terms of the observed velocity of descent and the torque required to rotate the piston. If the only leakage is past the piston, it is easily shown that this frictional force is negligible in the present investigation.

Let $V_1$ be the downward velocity of the piston, and $f_1$ the corresponding force, then substitution in equation (6) of $-V_1$ instead of zero for the velocity at the radius $r_1$ gives a value for $f$ exceeding that in equation (8) by the amount

$$f_1=\frac{2LV_1\pi\mu}{\log_e\frac{r_2}{r_1}}$$

or approximately

$$f_1=\frac{2LV_1r_1\pi\mu}{W}$$

The corresponding proportional error in the measured pressure is

$$\frac{f_1}{p\pi r_1^2}=\frac{2V_1L\mu}{pWr_1} \tag{29}$$

If the only leakage is past the piston

$$V_1=\frac{Q}{\pi r_1^2}$$

but from equation (15)

$$Q=\frac{\pi\ p\ W_2^3\ r_1}{6\ L\ \mu}$$

Substitution of these values in equation (29) gives, since $W_2$ and $W$ are interchangeable without appreciable error

$$\frac{f_1}{p\ \pi\ r_1^2}=\frac{W^2}{3\ r_1^2} \tag{30}$$

which for the gages used is less than 1 part in 10,000,000.

When leakage other than that past the piston is encountered, the percentage error in pressure measurement will be proportional to the total leakage as may be deduced from equation (29).

[14] Forsch. Arb. Ingenieurw., **48**, p. 1; 1907.

In the earlier pressure measurements, leakage from valves, etc., was considerably greater than that past the piston, but as time progressed extraneous leakage has been reduced, until recently it is much smaller than that past the piston. It seems fairly safe to say that the error from this source has never been more than 1 part in 100,000, since even this small error would correspond to a leakage 100 times as great as that past the piston, a rate which would have constituted a nuisance, due to the frequency with which the oil in the gage would have had to be replenished.

This discussion leads to the following conclusions: (1) For a coaxial piston and cylinder having the form of true geometric cylinders of revolution, the effective width of crevice, that is, the amount to be added to the piston diameter to obtain the effective diameter, is approximately the difference in radii of the piston and cylinder. (2) For such a piston and cylinder the width of crevice calculated from leakage or torque measurements is practically the same as the effective width. (3) Any irregularity in the crevice will cause the width calculated from the leakage measurements to be somewhat larger than the effective width. If the irregularity is axial, the width calculated from the torque measurements is the largest of the three; if circumferential, it is the smallest. The width defined by the effective area is essentially independent of circumferential variations in the width of crevice and varies with axial variations as indicated by equation (27). (4) The error due to the sinking of the piston in displacing oil leakage is entirely negligible.

These conclusions form a basis for the critical examination of the experimental data which will be presented. The methods used for measuring the width of crevice are as follows:

(1) Measurement of the rate of oil leakage; (2) rotation of the piston at a constant speed and use of a calibrated spring to measure the torque required; and (3) initial rotation of the piston and weights by hand, and determination of the retarding torque from observations of the speed, the deceleration, and the moment of inertia of the rotating system.

1. For the measurement of oil leakage a small amount of weighed absorbent cotton was placed around the upper end of the piston in an annular space previously wiped dry, the load was applied to the piston, and the piston rotated at the usual speed for a period of 10 minutes to an hour, the time being chosen so that the amount of leakage was usually between 0.05 and 0.2 g. The cotton was again weighed and the weight of the oil obtained as the difference of the two observed weights.

2. The torque required to rotate the piston at a constant speed was determined by replacing the regular driving spring by a calibrated spring of suitable strength and, by means of a scale and pointer, observing the stretch of the spring while the piston was rotated. Since the torque was not uniform, due in part to irregular motor speed, it was necessary to take the mean of readings at several different azimuths of the piston. The observations with gage 2–A were further complicated by the fact that the torque passed through a maximum as the piston turned through a certain azimuth, and, furthermore, this maximum was much larger every second revolution than for alternate revolutions. The observations which indicated such anomalous behavior were confirmed by observations of similar minima

in the electrical resistance of the oil film between the piston and the cylinder. The difficulties arising from variable motor speed led to the use of a third method for measuring the width of crevice.

3. The frictional torque which retarded the rotating system at a decelerating speed was measured by disconnecting the driving springs, giving the piston and weights an initial spin by hand and repeatedly observing the time and the angular position of the rotating system until the rotation ceased. For convenience in using equation (21) it is desirable to make these observations at equal time intervals, but to make the experimental procedure easier, the time was observed at which consecutive revolutions or groups of revolutions were completed as well as the time and angular position at which the rotation ceased. These data were plotted with time and revolutions as coordinates, a smooth curve was drawn through the points, and the values of the angular positions given by this curve at equal time intervals were tabulated. Then the following were calculated: (1) Differences between the consecutive tabulated values, (2) the quotients obtained by dividing each difference by the following difference, and (3) the Napierian logarithms of these quotients. These logarithms were used in equation (21) to calculate a series of values for the width of crevice, a mean of these values being considered as a single observation. The values of width obtained near the end of the spin were smaller than those obtained for the higher speeds and were neglected in calculating the mean.

Table 7 contains the results obtained by these three methods. The results for each gage are grouped together. Each of the values given is the mean of several individual observations. With the exceptions stated in footnotes to the table, an oil with a viscosity of about 0.5 poise was used to obtain these results.

TABLE 7.—*Measurements of the average width of crevice between piston and cylinder*

GAGE 1-A

| Date and gage No. | Method[1] | Load on gage (in kilograms) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 21 | 41 | 61 | 81 | 101 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| | | μ | μ | μ | μ | μ | μ |
| March, 1920 | 2 | 0.7 | ------ | 0.7 | ------ | ------ | ------ |
| | [2] 1 | ------ | ------ | 1.0 | ------ | ------ | ------ |
| July–August, 1923 | 1 | ------ | 2.2 | 2.4 | 2.5 | 2.6 | 2.6 |
| August, 1925 | 1 | ------ | 2.2 | ------ | 2.4 | 2.4 | 2.5 |

GAGE 2-A

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| February, 1926 | 1 | ------ | 1.4 | 1.3 | 1.2 | 1.1 | 1.1 |
| April–May, 1926 | 1 | ------ | ------ | 1.4 | 1.3 | 1.3 | ------ |
| | 2 | ------ | 1.3 | [3] 1.8 | .8 | .6 | ------ |
| June, 1926 | 1 | ------ | 1.7 | 1.7 | 1.6 | 1.5 | ------ |
| August, 1926 | 3 | ------ | .8 | .7 | .5 | .8 | ------ |
| August, 1927 | 1 | ------ | 2.0 | ------ | ------ | 1.8 | ------ |
| | 3 | ------ | .8 | .9 | .9 | .9 | ------ |

[1] Three methods were used: (1) Measurement of oil leakage, (2) measurement of torque by means of a calibrated spring, (3) measurement of torque by deceleration of the rotating system.
[2] Piston lapped twice in 1922.
[3] The mean of only three observations. If one observation is discarded, the mean is 1.4.

TABLE 7.—*Measurements of the average width of crevice between piston and cylinder*—Continued

GAGE 3-B

| Date and gage No. | Method | Load on gage (in kilograms) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 21 | 41 | 61 | 81 | 101 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| | | μ | μ | μ | μ | μ | μ |
| August, 1925 | 1 | ------- | 1.1 | 1.0 | 1.0 | 1.0 | 1.0 |
| March, 1926 | 1 | ------- | 1.0 | ------- | ------- | 1.0 | ------- |
| August, 1927 | 1 | ------- | ------- | .9 | ------- | .9 | ------- |
| | 3 | ------- | .8 | .8 | .8 | .8 | ------- |
| April, 1928 | 3 | ------- | .7 | ------- | .6 | ------- | ------- |
| | 1 | ------- | .8 | .8 | .8 | ------- | ------- |

GAGE 3-C

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| March, 1926 | 1 | ------- | 4.3 | ------- | ------- | ------- | ------- |
| July, 1927 | 3 | ------- | [4] 5.3 | ------- | ------- | ------- | ------- |
| | 1 | ------- | [5] 5.2 | 5.0 | ------- | ------- | ------- |

GAGE 4-C

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| February, 1926 | 1 | ------- | ------- | 1.0 | 1.0 | ------- | ------- |
| March, 1926 | 1 | ------- | 1.0 | ------- | ------- | 1.0 | ------- |
| July, 1927 | 1 | ------- | [6] 1.9 | 1.3 | ------- | ------- | ------- |
| March, 1928 | 3 | ------- | 1.4 | ------- | 1.0 | ------- | ------- |
| | 1 | ------- | 2.2 | ------- | 2.1 | ------- | ------- |

10-BAR GAGE

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1925 | 1 | ------- | 4.2 | ------- | 4.7 | ------- | ------- |
| May, 1928 | 1 | ------- | ------- | 4.2 | ------- | 4.4 | ------- |
| | 3 | ------- | 4.3 | 3.3 | 3.5 | 3.7 | ------- |

[4] Obtained with cylinder stock. The value obtained with renown engine oil was about 3.0.
[5] Obtained with both renown engine oil (viscosity at room temperature about 0.5 poise), and cylinder stock (viscosity about 11 poises).
[6] Piston sticking badly at this date. Piston was lapped in September, 1927.

The precision with which the crevice width was determined from the measurement of oil leakage was rather high, the average deviation of individual observations from the mean being the largest for gage 2–A, namely, about 5 per cent. The precision of the torque measurements was not so good, the average deviation from the mean being about the same for all the gages, namely, 20 to 25 per cent. The accuracy of the torque measurements for the 10-bar gage with a load of 21 kg is poor, because the time of spin was short and observations had to be taken rapidly.

For some of the gages the width of crevice determined by leakage measurements appears to change consistently with the pressure. It is difficult to say whether this variation is significant, but slight variations in either direction are explainable as follows: (1) If the load is slightly eccentric, the angle between the axis of the piston and that of the cylinder may be expected to change with the load, thus varying the uniformity of the crevice; (2) if the piston and cylinder are lapped

to fit more closely at the upper end than at the lower the application of pressure will cause the cylinder to stretch and the hollow piston to shrink, with a consequent increase in the average crevice width; and (3) if the piston and cylinder are lapped to fit more closely at the lower end than at the upper, the application of pressure will cause the reentrant part of the cylinder to shrink upon the solid portion of the piston with a consequent decrease in the average crevice width.

In Table 7 the values for crevice width obtained from torque measurements are, in general, appreciably less than those from leakage measurements. If the difference is caused by circumferential irregularities only, the effective width should be between the values given by the two methods; if there exists a combination of axial and circumferential irregularities, the effective width will be less than the value determined from leakage, but it may be either more or less than the value determined by torque measurements.

An attempt to determine the width of crevice by measurement of the electrical resistance across the oil film gave results much too small. The results indicated that either the voltage used (1 volt) had broken down the oil film, or that the piston was practically in contact with the cylinder at one or more spots.

It is now possible to compare the results obtained in the absolute calibration with those obtained by direct comparison with the mercury manometer. For this purpose, data from Tables 4, 5, and 7 have been correlated in Table 8, together with the values of piston diameter as measured with an interferometer. All values have been corrected to 20° C. In every case the upper of a pair of bracketed numbers was derived from measurements of leakage and the lower from those of torque. The values in column 3 have been chosen from Table 7 in such manner that they correspond chronologically as nearly as possible to the values in columns 2 and 6.

The importance of choosing observations which are approximately simultaneous is illustrated by the data on gage 3–C in 1927 and on gage 4–C in 1928. The two values for the diameter of the cylinder C which may be calculated from these data, with the assumption that the effective diameter is the mean of the piston and cylinder diameters, differ by over $3\mu$, indicating an increase in the diameter of cylinder C. This indication is confirmed by an analysis of the data in Tables 4, 5, and 7 for gage 4–C alone in the interval 1926 to 1928. Table 7 shows also that the diameter of piston No. 4 increased by $1\mu$ in excess of the unknown amount removed by lapping, and that the diameter of piston No. 3 decreased by about $2\mu$.

Table 8 indicates that torque measurements give a more nearly correct value of the average crevice width than do the leakage measurements, but even they lead to a value that exceeds the effective by as much as $1.0\mu$, the average excess being $0.5\mu$. That this difference is not entirely due to errors in crevice measurements is shown by the fact that the effective diameter for gage 3–B in 1928 is actually less than the measured piston diameter. In this particular instance the discrepancy must be attributed to one or both of two sources: (1) Error in pressure measurement, (2) error in the measurement of the piston diameter with an interferometer.

TABLE 8.—*Comparison of different methods for calibrating gages*

GAGE 2-A

| Gage number and date | Piston diameter | Crevice width | Column (2) plus column (3) | Area calculated from column (4) | Observed effective area | Column (5) minus column (6) | Observed effective diameter from column (6) | Column (4) minus column (8) |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| | *cm* | *cm* | *cm* | *cm²* | *cm²* | *cm²* | *cm* | *cm* |
| February, 1926 | 1.13197 | [1] 0.00014 | 1.13211 | 1.00662 | | 0.00012 | | 0.00007 |
| April–May, 1926 | | .00013 | 1.13210 | 1.00660 | | .00010 | | .00006 |
| March, 1926 | | | | | 1.00650 | | 1.13204 | |
| August, 1927 | | [1] .00020 | 1.13212 | 1.00664 | 1.00642 | .00022 | 1.13200 | .00012 |
| October, 1928 | 1.13192 | .00008 | 1.13200 | 1.00642 | | 0 | | 0 |

GAGE 3-B

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| April, 1922 | 1.12642 | | | | | | | |
| November, 1924 | 1.12643 | | | | | | | |
| March, 1926 | 1.12622 | [1] 0.00010 | 1.12632 | 0.99635 | 0.99629 | 0.00006 | 1.12629 | 0.00003 |
| August, 1927 | | .00008 | 1.12630 | .99632 | | .00003 | | .00001 |
| March, 1928 | | | | | .99612 | | 1.12619 | |
| April, 1928 | | [1] .00008 | 1.12630 | .99632 | | .00020 | | .00011 |
| October, 1928 | 1.12622 | .00007 | 1.12629 | .99630 | | .00018 | | .00010 |

GAGE 3-C

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| June, 1927 | | | | | 0.99676 | | 1.12655 | |
| July, 1927 | | [1] 0.00052 | 1.12674 | 0.99710 | | 0.00034 | | 0.00019 |
| October, 1928 | 1.12622 | .00042 | 1.12664 | .99692 | | .00016 | | .00009 |

GAGE 4-C

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| March, 1926 | [2] 1.12692 | | | | [3] 0.9972 | | 1.1268 | |
| March, 1928 | | [1] 0.00022 | 1.12725 | 0.99800 | .99777 | 0.00023 | 1.12712 | 0.00013 |
| October, 1928 | 1.12703 | .00014 | 1.12717 | .99786 | | .00009 | | .00005 |
| | Mean difference using leakage measurements | | | | | .00020 | | .00011 |
| | Mean difference using torque measurements | | | | | .00009 | | .00005 |

[1] The values in this row were obtained from leakage measurements and those in the next row from torque measurements.
[2] Piston lapped between the observation marked and the next observation.
[3] The piston was sticking badly. Piston was lapped September, 1927.

1. The estimated error which may occur in the use of the manometer is discussed in detail later, and is about the same as the discrepancy in area mentioned; that is, a little less than 1 part in 10,000, or less than 0.5 $\mu$ in the diameter of an 11 mm piston.

2. The measurement of piston diameter with an interferometer is capable of much greater accuracy than the irregularities in diameter permit. The total estimated error, including that due to any uncertainty in the temperature during measurement, is about 0.2$\mu$ for the

11 mm pistons (Nos. 1, 2, 3, and 4) and about 0.5 $\mu$ for the 35 mm piston (No. 5, 10-bar).

We may conclude that the use of leakage measurements in the absolute calibration gave a calculated effective area slightly too large, especially for gages with crevices over 1 or 2 $\mu$ in width, but that the use of torque measurements in the absolute calibration gave results which, for the gages observed, were about as accurate as those obtained from a comparison of the gages with the manometer described, the difference between the effective areas obtained by the absolute calibration and the comparison with the manometer being less than 2 parts in 10,000. For gages having larger and more irregular crevices a comparison with the manometer appears preferable to an attempt at absolute calibration, since for such gages the torque might be less accurately measurable. Furthermore, the direct comparison with the manometer gives a better indication of the accuracy and precision which may be expected of the gage in actual pressure measurements.

## VIII. SOURCES OF ERROR IN MANOMETER AND GAGES

Sources of error arising from the use of the manometer are as follows:

1. *Graduation of scales and observation of reading devices.*—The error of graduation of the manometer scales does not exceed 0.04 mm. When oil was used as a pressure-transmitting liquid, the precision obtained with the manometer was limited by the inability of the observer to locate the mercury surfaces within about 0.5 mm. With the use of alcohol the uncertainty was reduced to 0.1 or 0.2 mm; with the use of water, to about 0.05 mm. In consequence, the combined error for the 10 water-mercury menisci will not exceed 1 mm, while the probable error will be about 0.3 mm, or 2 parts in 100,000.

2. *Error in temperature measurement.*—It is believed that the thermometer indicates the temperature of the manometer within 0.2° C., which corresponds to 4 parts in 100,000 in the pressure measurement.

3. *Capillary forces.*—For the observations taken in 1926 and in December, 1925, the heights of the mercury menisci were observed and correction was made for capillary forces, with the aid of certain data [15] and assumptions. The assumption that the correction for a mercury-water meniscus would be three-fourths of that for a mercury-air meniscus was made by inference from a paper by F. R. Watson [16] which gives the interfacial tension between mercury and water as about three-fourths of the surface tension of mercury.

The corrections for capillary forces rarely amounted to as much as 0.04 cm, positive corrections being about equal in number and amount to negative. Consequently, although the application of these corrections reduced the average deviation from the mean to about 0.8 of what it would have been if the corrections had not been applied, it did not appreciably change the mean values.

The observations made in 1927 and 1928 were not corrected in this manner, but the manometer tubes were tapped so as to disturb the mercury surfaces rather violently two or three times before readings were taken. The data in Table 4 show that the average deviation

[15] Physikalisch-Chemische Tabellen, Landolt-Bornstein-Roth, 5th ed., p. 72.
[16] Phys. Rev., **12**, p. 257; 1901.

from the mean values is about the same as for the observations in 1926, or that the tapping produced close reproducibility of form in all the mercury surfaces. In view of the uncertainty of capillary errors it is advisable to make observations in tubing of such size that the errors are negligible. The tubing of the 15-bar manometer fulfills this condition within the accuracy intended by the designer, but the accuracy required of this instrument has been considerably increased during its years of use.

Equations for estimating the diameter of tube corresponding to a capillary correction smaller than a specified amount have been developed mathematically by Laplace and by Lord Rayleigh.[17] The equations apply accurately only to narrow tubes or to those having diameters of 4 cm or more, but give an approximate estimate for intermediate sizes.

4. *Lack of equilibrium.*—The program of observation has been carried out in such manner that errors due to this source are probably negligible.

It is believed that the combined effect of these errors will not be greater than 1 part in 10,000, and that the manometer is accurate within that limit.

The use of the piston gages is accompanied by the following sources of error:

1. *Change in the dimensions of the piston or cylinder.*—Change in the dimensions of the steel in the gages has been the source of considerable trouble; not only has it caused a decrease of 2 or 3 parts in 10,000 in the effective area of gage 3–B, but it has necessitated a relapping of cylinder A, piston 4, and the piston of the 10-bar gage, to relieve sticking. The changes consisted of a bending of the axis of cylinder A, an increase in the diameter of piston 4, as well as its cylinder C, and a change from circular to elliptic cross section in the piston of the 10-bar gage.

2. *Sticking of the piston.*—No definite value can be assigned to the error due to this cause. In the procedure followed for calibration of the gages, any error of this nature would appear as a part of the variation in the results. The maximum variation of the data in Table 6 for a comparison between gages 3–B and 4–C is 6 parts in 100,000, while data from a comparison of 4–C with the manometer before the piston was lapped to relieve sticking showed variations as large as 2 parts in 1,000.

3. *Error in temperature measurement.*—The thermometers used at present probably measure the temperature of the gage within 0.3° C., which corresponds to an error of less than 1 part per 100,000. The accuracy of this temperature measurement could be improved easily should the need for such improvement arise.

4. *Magnetic forces.*—Data for gage 2–A given in Table 4 under date of June and July, 1926, show that the error due to the magnetic field of the motor is not greater than the precision of the results, about 3 parts in 100,000. The motor which rotates the piston in base 12,083 is farther removed from the other iron parts of the gage than the motor on base 30213. Consequently, the results with base 12083 and with the motor removed from its normal position in base 30213

[17] Scientific Papers by Lord Rayleigh, **6**, p. 350, published by Cambridge Univ. Press; or Proc. Roy. Soc. A, **42**, p. 184; 1915.

should be less subject to error than the results with the motor in its normal position on base 30213.

5. *Lack of equilibrium.*—Errors due to this cause have been made negligibly small by allotting sufficient time to each observation.

6. The vertical component of the force applied to rotate the piston may be neglected, since it is not over a few hundredths of a gram.

The most important source of error in measurements with the piston gage appears to be a secular change in the dimensions of steel, which may amount to 3 or 4 parts in 10,000 in the effective area. With calibrations sufficiently frequent to correct for this change, an accuracy better than 1 part in 10,000 may be attained.

## IX. ACKNOWLEDGMENTS

The authors are indebted for advice and suggestions from Dr. H. C. Dickinson and E. F. Mueller, under whose supervision this investigation was made.

The high quality of workmanship in the piston gages is due to the skill of F. Knoop, G. W. Bicking, jr., and the late H. K. Harring, who constructed the gages and lapped the pistons and cylinders, when necessary on account of changes in dimensions.

The authors are indebted to C. G. Peters, who made repeated measurements of the pistons with an interferometer, thereby assisting in the construction of pistons with uniform diameters and giving data on the diameters at various intervals after the gages had been constructed.

## X. SUMMARY

The results of the work with the multiple U tube manometer and the group of piston gages maintained for the precise measurement of pressures may be summarized as follows:

Oil, alcohol, and water have been used successively to transmit the pressure between the manometer tubes. Of these, water has been found to be the most satisfactory.

The results emphasize the necessity of using tubing of such size at the mercury menisci that capillary forces are negligible.

The mercury manometer is capable of an accuracy within 1 part in 10,000. On account of secular changes in the dimensions of steel, the piston gages require occasional calibration when an accuracy within 3 or 4 parts in 10,000 is desired. The precision obtained for the direct comparison of two piston gages indicates that with the elimination of secular changes, or with sufficiently frequent comparison with a manometer of the requisite accuracy, these gages would be accurate within 3 or 4 parts in 100,000.

The rotational speed of the piston had no measurable effect upon the effective area of the gage.

The change in effective area with pressure, in the range 0 to 75 bars, was less than the precision of measurement, about 3 parts in 100,000, or about 1 part in 2,000,000 per bar. The effective radius is slightly smaller than either the mean of the radii of the piston and cylinder or the radius corresponding to the mean of the areas of piston and cylinder, but for all practical purposes the three values are equal.

The measurement of piston diameter with an interferometer and the determination of crevice width from measurements of oil leakage

or of torque, furnish data for the calibration of the piston gage as a primary instrument. For the gages described, such calibrations agree with the results of comparisons with the manometer within 2 or 3 parts in 10,000 of the effective area, the calibration by means of torque being the better, though not quite so reproducible as that by leakage. Direct comparison with the manometer is desirable, since it indicates also the accuracy and precision which may be expected of the gage in actual pressure measurements.

A list or references to papers on the subject of differential manometers and piston gages is given in the Appendix at the end of this paper. The titles of the papers have been omitted and brief abstracts of the contents have been given instead, since some of the titles do not indicate the presence of the data on this subject.

## XI. APPENDIX

[A list of references to papers on the subject of differential manometers and piston gages]


1. Richard, Ann. Mines, **7,** p. 481; 1845. (A multiple tube manometer for pressures up to 7 atmospheres is described.)
2. V. Regnault, Relation des Experiences., **1,** p. 343; 1847. (A single column manometer for pressures up to 30 atmospheres is described.)
3. L. Seyss, Dingler's Polytech. J., **191,** p. 352; 1869. (A piston gage with two pistons, one inside the other, is described. The weights are so arranged that when the piston rises it picks up one weight at a time.)
4. Desgoffe, Dingler's Polytech. J., **202,** p. 393; 1871. (Illustrated description of a piston gage. The measured pressure forced a small piston downward against a larger piston which rested upon a diaphragm. The flexure of the diaphragm forced mercury upward in a glass tube. A calibrated scale behind this tube was graduated to read pressures directly.)
5. L. Cailletet, Compt. rend., **84,** p. 82; 1877. (A single column manometer for pressures up to 34 atmospheres is described.)
6. E. H. Amagat, Compt. rend., **87,** p. 432; 1878. (A single column manometer 300 m high at Lyon is described.)
7. L. Cailletet, Ann. chim. phys. (ser. 5), **19,** p. 386; 1880. (Description of a piston gage. The space between the piston and cylinder was not more than 0.01 mm. The leakage of water past the piston was stopped by goldbeater's skin. The piston was held down by a lever loaded with weights.)
8. M. Thiesen, Z. Instrumentenk., **1,** p. 114; 1881. (A proposed multiple tube manometer using water as a pressure transmitting fluid is described.)
9. E. Ruchholz, Dingler's Polytech. J., **247,** p. 21; 1883. (Illustrated description is given of a piston gage in which the weight pan was rigidly attached to the upper end of the piston. No packing around the piston is shown or mentioned.)
10. E. H. Amagat, Compt. rend., **103,** p. 429; 1886. (Description of a gage similar to that in reference No. 4, except for the omission of packing around the small piston and the diaphragm under the large piston with a closer fit between pistons and cylinders. Molasses was used in the high pressure cylinder and castor oil in the low pressure.)
11. P. G. Tait, Nature, **41,** p. 361; 1890. (A gage similar to the preceding one is briefly described.)
12. E. H. Amagat, Ann. chim. phys. (ser. 6), **29,** p. 70; 1893. (Illustrated description of gage similar to that in reference No. 10. The small piston and cylinder were of tempered steel, the large cylinder of bronze.)
13. Michael Altschul, Z. phys. Chem., **11,** p. 583; 1893. (A piston gage with design similar to that in reference No. 9 is briefly described. A steel cylinder and bronze piston were used.)
14. Physikalisch-Technische Reichsanstalt, Z. Instrumentenk., **13,** p. 125; 1893. (Announcement of completion of the manometer proposed by Thiesen, reference 8.)
15. S. W. Stratton, Phil. Mag., **38,** p. 160; 1894. (A short note proposing the use of a multiple tube manometer.)
16. Phys.-Tech. Reich., Z. Instrumentenk., **14,** p. 307; 1894. (Description of Stückrath's pressure balance with packing of goldbeater's skin, and results of comparison with manometer are given. The precision obtained was about 5 per cent.)
17. L. Cailletet, Compt. rend., **112,** p. 764; 1894. Z. compr. fluss. Gase Pressluft-Ind., **1,** p. 88; 1897. (A single column manometer 300 m high on the Eiffel Tower is described. The main column of mercury was inclosed in a steel tube to which glass branch tubes were attached through metal stopcocks at intervals of 3 m. The temperature of the manometer was calculated from the resistance of the telephone wire running parallel to it.)

18. H. F. Wiebe, Z. compr. fluss. Gase Pressluft-Ind., **1,** pp. 8, 25, 81, 101; 1897. (A series of papers gives, respectively (1) a brief history of manometers, and piston gages and an illustrated description of the multiple manometer at the Phys.-Tech. Reich.; (2) procedure for calculating pressures from observations of the manometer; (3) description of the Amagat gage invented by Gally-Cazalat and of the Stückrath pressure balance; (4) discussion of the precision of the Stückrath gage, about 2 parts in 1,000.)
19. H. Kamerlingh Onnes, Comm. Phys. Lab. Univ. Leiden No. 44; 1898. (The paper describes in detail a multiple tube manometer consisting of 15 U tubes for pressure differences up to 60 atmospheres and total pressures up to 100 atmospheres. A gas is used for transmitting the pressure.)
20. Jacobus, Engineering, **64,** p. 464; 1897, Z. Instrumentenk., **18,** p. 56; 1898. (A piston gage for pressures up to 1,000 atmospheres is described. The instrument was designed so that the load could be applied by means of platform scales or a testing machine.)
21. C. J. Schalkwijk, Comm. Phys. Lab. Univ. Leiden No. 70; 1901. (The various corrections to be applied and the accuracy of the manometer in reference No. 19 are discussed.)
22. Anonymous, Engineering, **75,** p. 31; 1903. (The paper gives an illustrated description of a piston gage at the National Physical Laboratory for pressures up to 10 tons per square inch. Comparison with a 50-foot manometer is mentioned.)
23. E. Wagner, Ann. Physik (ser. 4), **15,** p. 906; 1904. (Describes a Stückrath pressure balance and an Amagat gage. These gages were taken apart, the piston diameters measured, and the average cylinder diameters determined from the weight of mercury required to fill them. For the determination of the effective area the unmounted cylinders were attached to a manometer about 1.5 m high, and weights were piled on a cork disk rigidly attached to the upper end of the piston.)
24. L. Holborn and F. Henning, Ann. Physik (ser. 4), **26,** p. 833; 1908. (A part of a paper on the vapor pressure of water describes the 12 m single-column mercury manometer at the Phys.-Tech. Reich. The main column of mercury was inclosed in a steel tube to which glass branch tubes were attached through metal stopcocks at intervals of 2 m. The temperature of the manometer was determined from the resistance of a nickel wire parallel to the manometer and inclosed in the same housing. The corrections applied for the calculation of pressures are discussed.)
25. A. Martens, Z. Ver. deut. Ing., **51**$_2$, p. 1184; 1907. (The paper discusses the effect of friction from packings upon the accuracy of the measurement of force with hydraulic presses. The effect was 7 to 23 per cent at 5 atmospheres and 1 or 2 per cent at 200 atmospheres. Curves showing the variation of the effect with pressure are given.)
26. P. W. Bridgman, Proc. Am. Acad. Arts Sci., **44,** p. 199; 1908–9; Phys. Rev., **28,** p. 145; 1909. (A piston gage with a packed $\frac{1}{16}$-inch hardened steel piston is described. The gage was sensitive to 2 kg per cm$^2$ at a pressure of 7,000 kg per cm$^2$.)
27. George Klein, Dissertation Kön. Tech. Hochschule Berlin September, 1908. A slightly abbreviated article is given in Z. Ver. deut. Ing., **54,** p. 791; 1910. (The paper gives a comparison with a manometer of several piston gages, including gages designed by Stückrath, Martens, Schaeffer and Budenberg. The author discusses sources of error of these gages and determines their sensitivity. Small holes were bored along a line parallel to the axis of an experimental cylinder and the pressure at these holes measured.)
28. A. Martens, Z. Ver. deut. Ing., **53,** p. 747; 1909. (The paper describes and illustrates various possible designs of gages as well as two gages constructed by Martens.)
29. P. P. Koch and E. Wagner, Ann. Physik (ser. 4), **31,** p. 31; 1910. (The paper describes a single-column manometer built in a 25 m tower at the University of Munich, and gives the results of a comparison of a gage similar to Amagat's with this manometer. The gage is sensitive to 0.004 atmospheres at 30 atmospheres.)
30. L. Holborn and A. Baumann, Ann. Physik, **31,** p. 945; 1910. (A portion of this paper on the vapor pressure of water gives an illustrated description of the piston gage used. The cylinder was of bronze. The steel piston was given an oscillatory rotation to avoid sticking.)

31. H. F. Wiebe, Z. Kompr. fluss. Gase Pressluft-Ind., **13,** p. 83; 1910. (A history of pressure gages and manometers is given. The piston gages built by Stückrath for the Phys.-Tech. Reich. are described. The older type was given an oscillatory rotation, while the newer type were rotated by a worm wheel. The cylinder and piston were made of 25 per cent nickel steel. Cup-shaped packings of goldbeater's skin were used. Precision of measurement was about 1 part in 1,000.)
32. L. Holborn and H. Schultze, Ann. Physik (ser. 4), **47,** p. 1089; 1915. (This portion of a paper on the isotherms of air, argon, and helium describes the method used to calibrate the two piston gages for pressures up to 100 atmospheres. One gage was connected to each end of a 12 m differential manometer described in reference 24 and a comparison made at pressure intervals of about 15 atmospheres. By making comparisons also with the gages interchanged the effective area of either gage at a given pressure could be used to calculate the effective area of the other at the next higher pressure.)
33. C. A. Crommelin and Miss E. I. Smid, Comm. Phys. Lab. Univ. Leiden No. 146c; 1915. (A comparison of a Schaeffer and Budenberg gage with a differential manometer at pressures up to 100 atmospheres is described. Two closed end manometers of 60 and 120 atmosphere capacity were compared with the differential manometer, and the piston gage was compared with these. The effective area was found to increase 2 parts per 1,000 up to 70 atmospheres and to decrease about the same amount from 70 to 100 atmospheres.)
34. F. G. Keyes and R. B. Brownlee, Thermodynamic Properties of Ammonia, p. 10, published by John Wiley & Sons. (A brief description of a piston gage and its calibration is given.)
35. F. G. Keyes and R. B. Brownlee, J. Am. Chem. Soc., **40,** p. 25; 1918. (A part of a paper on the vapor pressure of ammonia in which is a brief illustrated description of a piston gage and its calibration.)
36. L. Holborn, Z. Ver. deut. Ing., $\mathbf{67_1}$, p. 188; 1923. (A brief illustrated description of the piston gage at Phys. Tech. Reich.)
37. A. Michels, Ann. Physik, **72,** p. 285; 1923. (The paper gives a theoretical discussion on the effect of rotation upon the sensitivity of piston gages as well as data obtained from observation of both the deceleration of the freely rotating piston and the electrical resistance of the oil film between the piston and cylinder. Both sets of data indicated that above a certain critical speed there was a continuous oil film between the piston and cylinder. An illustrated description is given of the gage used, which was of the Schaeffer and Budenberg type. The piston was rotated continuously in one direction.)
38. A. Michels, Ann. Physik, **73,** p. 577, 1924. (This paper describes the comparison of the gage mentioned in the preceding reference with a 9 m single-column mercury manometer. With the aid of a closed-end hydrogen manometer also compared with the differential manometer, the comparison was made at pressures up to 175 atmospheres. The effective area of the gage was found to be constant within the limits of experimental error, 1 part in 3,000. A theoretical discussion indicates that the effective area of the gage should not change more than 1 part in $4 \times 10^6$ per atmosphere.)
39. L. Holborn, Handbuch der Experimental Physik, **1,** Messmethoden, p. 63, published by Akademische Verlagsgesellschaft m. b. H., Leipzig; 1926. (A chapter of this book gives an illustrated description of several pressure gages at the Phys.-Tech. Reich.)
40. H. Ebert, Handbuch der Physik, **2,** chapter 8A, published by Julius Springer; 1926. (This chapter is devoted to the production and measurement of pressures. A history of the subject is given as well as a description of several manometers and gages, and discussion of their accuracy.)
41. F. G. Keyes, Mech. Eng., **49,** p. 163; 1927. (A short report on the calibration of the pressure gages at the Mass. Inst. of Tech. This subject is covered more in detail in the next reference.)
42. F. G. Keyes and Jane Dewey, J. Optical Soc. Am., **14,** p. 491; 1927. (The method used by Holborn and Schultze was followed to compare piston gages with a single column manometer at pressures up to 587 atmospheres. The effective area of the gage with the larger piston did not change more than 1 part in 40,000 for pressures up to 160 atmospheres; that of the gage with the smaller piston increased about a part in 11,000 when the pressure was increased from 0 to 587 atmospheres.)

43. E. P. Bartlett, H. L. Cupples, and T. H. Tremearne, J. Am. Chem. Soc., 50, p. 1275; 1928. (A portion of a paper on the isotherms of nitrogen and hydrogen in which appears an illustrated description of two piston gages in use at the Bureau of Chemistry, Department of Agriculture.)

Washington, March 11, 1931.

# THE WAIDNER-BURGESS STANDARD OF LIGHT

By H. T. Wensel, Wm. F. Roeser, L. E. Barbrow, and F. R. Caldwell

ABSTRACT

A source of light sufficiently reproducible to serve as a fundamental photometric reference standard has been obtained by carrying out the original suggestion of Waidner and Burgess to immerse a hollow inclosure in a bath of molten platinum and to make observations during the period of freezing.

The platinum, of exceptionally high purity, was contained in thorium oxide crucibles and was heated by means of a high-frequency induction furnace. The brightness of the source, reproducible to 0.1 per cent, was 58.84 international candles per square centimeter.

The platinum used was not appreciably contaminated by being melted and frozen over 100 times in crucibles of fused thorium oxide. Various tests indicated that the platinum was at all times purer than 99.997 per cent.

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## I. EXISTING UNITS AND STANDARDS

Since visible light, by its very definition, involves physiological and psychological reactions, it is not possible to derive a unit of light from the units of a purely physical system. To measure light, an arbitrary unit must be established, in addition to the arbitrary units upon which a physical system may be based. For example, a unit of luminous intensity might be defined as the light corresponding to radiation of a specified spectral distribution or quality and of a specified energy flux per unit solid angle. Such a unit would have the appearance of being derived from those of the physical system, but light is of such a nature that the derivation has no special significance, the practical value of the unit depending solely upon its reproducibility.

At present there are no means available for determining radiant energy quantitatively with an accuracy approaching that desired in modern photometry. Consequently, instead of describing the radiant energy, we are obliged to fall back upon a specification of the source which produces it. Any light source, therefore, which is reproducible from specifications, and which consequently emits visible radiation

the quantity and quality of which are fixed by such specifications, may be used as a fundamental reference standard. As another consequence of the nature of light, any such standard defines a unit of only limited applicability, in that it can be used to evaluate light of any other spectral distribution only by introducing an additional specification regarding the relative weights to be assigned to radiations of various wave lengths. Fortunately, such a specification, in the form of a table of visibility factors, has already been adopted by the International Commission on Illumination.[1]

Beginning with the sperm candle defined in the British metropolitan gas act of 1860, a large number of standards, more or less reproducible from specifications, have been proposed and some of them adopted. The most widely used have been the Pentane lamp, described by H. E. Vernon Harcourt [2] in 1877 and the Hefner lamp devised by F. von Hefner Alteneck [3] in 1884. These flame standards are not, however, satisfactory, first because the lamps themselves are not accurately reproducible, and second because their light output is dependent to a great extent on atmospheric conditions which can not be controlled with sufficient accuracy.

A standard entirely different in principle was proposed by Violle.[4] This standard is a luminous surface of platinum at its freezing point, the light from 1 square centimeter of which is called the Violle. It seemed to give promise of ending the search for a satisfactory reproducible standard and was adopted by the International Electrical Congress in 1889, the one-twentieth part of the Violle being given the name "Bougie décimale." However, this standard proved to be even less reproducible than the flame standards. The presence of a slight amount of foreign material on the surface greatly affects the amount of light emitted. Moreover, it was found by Burgess [5] that the emission from incandescent platinum has a well-marked discontinuity at the freezing point, a decrease of some 15 per cent for red light occurring upon freezing without change in temperature. Whatever the cause, published values [6] for the light emitted by the Violle standard differ by over 20 per cent from the originally assigned value.

No fundamental reference standard reproducible accurately enough for the purposes of modern photometry has been available and no one primary standard has been universally accepted. In 1909 the then existing units of candlepower of Great Britain, France, and the United States were brought into agreement [7] and the resultant unit was termed the international candle. Germany and the other countries which had previously adopted the Hefner standard continued to use the unit derived therefrom, but its value was accepted as being 0.9 of the international candle. The international unit has since then been maintained by means of carbon-filament lamps deposited in the various national laboratories. While these lamps have for the present the status of primary standards, it was recognized at the time that their adoption was only a temporary expedient and that they would in time be superseded by some reproducible standard.

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[1] Recueil des Travaux, I. C. I. 6th session, p. 67, Geneva; 1924. See also B. S. Sci. Papers, **19**, p. 131; 1923-24. Trans. Illum. Eng. Soc., **19**, p. 176; 1924; and **20**, p. 629; 1925.
[2] B. A. Report, p. 845; 1898.
[3] E. T. Z., **5**, p. 20; 1884.
[4] C. R., **88**, p. 171; 1879; Ann. de Chim. et Phys., **3**, p. 373; 1884.
[5] B. S. Bull., **2**, p. 591; 1914.
[6] Zs. f. Instrk., **11**, p. 161; 1891; **14**, p. 267; 1894.
[7] B. S. Circular No. 15; 1909.

## II. BLACK-BODY RADIATION STANDARDS

In 1908 Waidner and Burgess [8] suggested as a standard of light a black body immersed in a bath of freezing platinum. This suggestion retained the one desirable feature possessed by the Violle standard, namely, a reproducible temperature at which to operate the radiator, and at the same time avoided the variations arising from the character of the radiating surface. This suggestion received much favorable comment, but it was many years before any serious attempt was made to realize the standard in practice.

In 1924, Ives [9] set up a light source somewhat along the lines of the Waidner-Burgess suggestion. He fashioned cylinders of platinum foil, the ends of which were clamped in heavy terminals. An electric current passing through the platinum was regulated so as to bring the temperature up slowly to the point where the cylinders melted. A longitudinal slit in the platinum foil permitted the light from the interior "black body" to emerge and to be compared with other light sources. Although Ives did not realize the standard of Waidner and Burgess, he perfected a source which was reproducible to a higher degree than any previously devised. For the brightness of this source Ives obtained a value of 55.40 candles per square centimeter.

In 1926, Brodhun and Hoffmann [10] set up a black-body furnace, the temperature of which was determined by the fusion of a small bit of pure platinum welded between the hot junctions of a 90 Pt–10 Rh to 60 Pt–40 Rh thermocouple. The melting of the pure platinum manifested itself in a slight halt in the emf.-time curve of the thermocouple, so that observations, made slightly before and slightly after the thermocouple indicated the melting temperature, could be corrected by means of the thermocouple readings. The result obtained by these workers was 65.24 Hefners per square centimeter, which, on the basis of the conversion factor 0.9, is equivalent to 58.72 international candles per square centimeter. Comparisons of candlepower of carbon-filament standard lamps made between the Physikalisch-Technische Reichsanstalt and the National Bureau of Standards during the last decade have been somewhat discordant, but on the whole have indicated that the ratio of the Hefner unit to the candle as maintained at the bureau is somewhat less than 0.9. Measurements made on a group of lamps in 1926 gave a ratio of 0.893. On this basis the result obtained by Brodhun and Hoffmann is equivalent to 58.26 candles per square centimeter.

Since Brodhun and Hoffmann used resistance furnaces wound with iridium and with a platinum-iridium alloy, the platinum melt sample was subject to contamination by iridium. A platinum wire which was allowed to remain in the furnace at a temperature near the melting point of platinum was found after some time to have undergone a marked change in thermoelectric properties in a direction to indicate the addition of iridium. Another source of error lies in the fact that it is practically impossible to secure temperature uniformity in a resistance-wound furnace. No estimate is given of the temperature differences existing within the furnaces used by Brodhun and Hoff-

[8] Elec. World, **52**, p. 625; 1908.
[9] J. Frank. Inst., **197**, p. 147; 1924. Also Rec. des Travaux I. C. I. Geneva, p. 77; 1924.
[10] Zeits f. Phys., **37**, p. 137; 1926.

mann. They merely state that the reading of the thermocouple depended on its location in the furnace.

The contamination of the platinum specimen by iridium is perhaps of no great consequence, since each specimen is in the furnace only for the length of time required to make one run. The temperature differences within the furnace present a more serious difficulty. Brodhun and Hoffmann observed the light coming from a small auxiliary hollow inclosure within the furnace, the thermoelement and bit of platinum being behind the back wall of this small cavity. The remarkably consistent results obtained in this work do not necessarily indicate that the specimen of platinum and the inner black body were at the same temperature, since a constant difference in temperature would likewise yield consistent results. In any case the question remains whether the conditions existing in the furnaces used in this work could be reproduced in furnaces constructed in other laboratories.

Fleury [11] and Chappius [12] have been working with a black body, the temperature of which is defined by the ratio ($N$) of its radiation (at wave length 0.622 $\mu$) to that of a black body held at the gold point. The ratio is measured by means of a spectrophotometer and a sector disk. For a radiator matching in color the carbon filament standard lamps $N$ lies between 450 and 470. The precision is estimated at better than 1.4 per cent.

Since in the source used by Ives only a comparatively narrow ring is at the melting point, much of the light emitted comes initially from colder portions of the tube. It was to be expected, therefore, that the value obtained by Brodhun and Hoffmann for a black body within a furnace would be somewhat higher than the value obtained for the brightness of the platinum cylinder source, but the large difference actually found was somewhat disturbing. This difference showed the necessity for further experimental work, and when such was undertaken at the National Bureau of Standards in July, 1928, it was decided to set up a source in exactly the manner suggested by Waidner and Burgess, namely, to immerse a black body in a bath of molten platinum and to take observations during the time the platinum is solidifying.

## III. APPARATUS AND METHODS

### 1. THE FURNACE AND CRUCIBLE

In the present work especial attention was given to the elimination of the two possible sources of error which may have been present in the work of Brodhun and Hoffmann, contamination of the platinum by metallic vapors and lack of temperature uniformity. The use of an induction furnace to generate the heating currents in the platinum itself eliminated all the usual sources of contamination with the exception of the refractories used to hold the platinum and to provide thermal insulation.

The uniformity of temperature, which was sought by immersing the black body in molten platinum, was further promoted by the violent stirring in the metal which results from the action of the

[11] Ann. de Phys. et de Chimie, **5**, p. 265; 1926.
[12] Proc. I. C. I. Saranac Inn, pp. 1102 and 1109; 1928.

magnetic field of the coil of the induction furnace on the currents induced in the metal. Thus when the metal is allowed to cool slowly without entirely cutting off the power supplied to the furnace, a practically uniform temperature within the metal is assured at the instant solidification begins.

The arrangement of crucible, immersed black body or sight tube, insulation, and platinum is shown in Figure 1 and a photograph of a

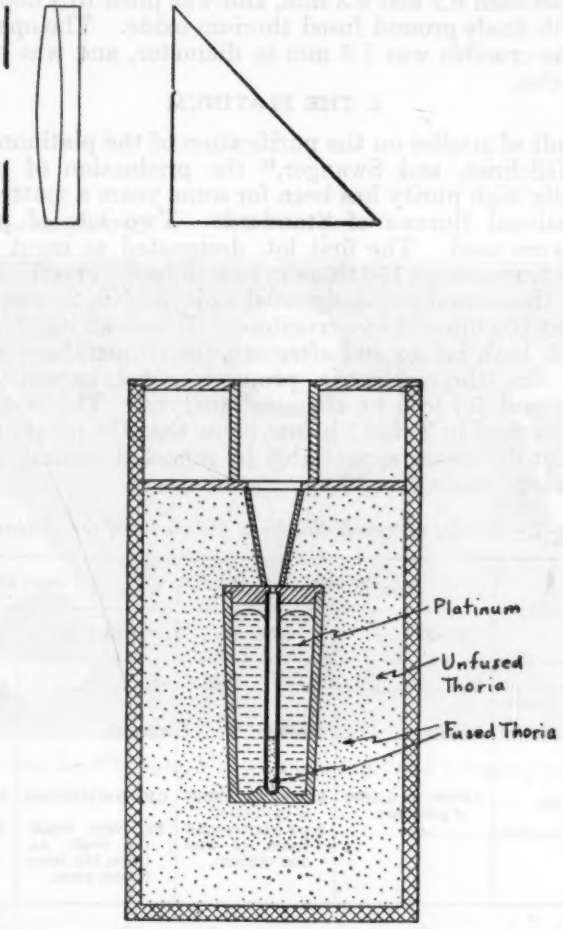


FIGURE 1.—*Cross section showing the platinum crucible and insulation*

cut-away view of the assembly in Figure 2. The crucible and sight tube, as described elsewhere in this journal,[13] were made of fused thorium oxide. They were surrounded by two layers of the same material, the inner layer being fused and ground and the outer unfused. The unfused material provides the greater part of the thermal insulation, but it is subject to a large shrinkage upon heating to high

[13] B. S. J. of Research, 6, p. 1131; 1931.

temperatures. The purpose of the fused material next to the crucible is to prevent leakage of the platinum through cracks which develop in the crucible. No trouble was experienced due to cracking of the sight tubes because of the slight temperature gradient through them.

The inside dimensions of the crucibles were substantially as follows: Diameter at the top 22 mm, diameter at the bottom 17 mm, height 45 mm. The sight tube had an inside diameter of 2.5 mm, a wall thickness between 0.2 and 0.3 mm, and was filled to a depth of about 15 mm, with finely ground fused thorium oxide. The opening in the cover of the crucible was 1.5 mm in diameter, and was coaxial with the sight tube.

### 2. THE PLATINUM

As a result of studies on the purification of the platinum metals by Wichers, Gilchrist, and Swanger,[14] the production of platinum of exceptionally high purity has been for some years a matter of routine at the National Bureau of Standards. Two lots of platinum so prepared were used. The first lot, designated as ingot No. 1, was melted and frozen some 150 times in four different crucibles of thorium oxide, and the second lot, designated as ingot No. 2, was melted and frozen about 100 times in two crucibles. These two ingots of platinum were tested, both before and after use, for temperature coefficient of resistance, for thermoelectric properties, for impurities spectrographically and for iron by chemical analysis. The results of these tests, summarized in Table 1 below, show that the purity of the platinum was not decreased appreciably by repeated melting and freezing in the thorium oxide crucibles.

TABLE 1.—*Results of tests indicative of the purity of the platinum used*

| Criterion of purity | Ingot No. 1 | | Ingot No. 2 | |
|---|---|---|---|---|
| | Before use | After use | Before use | After use |
| Emf. (microvolts at 1,200° C.), *v.* Standard platinum. | 33 | 89 | 46 | 51. |
| Temperature coefficient of resistance $\frac{R_{100}-R_0}{100\ R_0}$. | 0.003918 | 0.003903 | 0.003915 | 0.003904. |
| Chemical analysis | 0.99998 to 0.99999 of platinum. | 0.99997 to 0.99998 of platinum. | 0.99998 of platinum. | 0.99997 to 0.99998 of platinum. |
| Spectrographic analysis | | Spectroscopic traces of iron and calcium. | Fe, very weak; Ca, weak; Al, trace; Mg, trace; others, none. | Fe, very weak; Ca, weak; Al, trace Mg, none?; others, none. |

While the thermoelectric test is, perhaps, the most sensitive that can be applied in the detection of impurities, the temperature coefficient is generally recognized as the surest guide since small amounts of any impurity will lower the temperature coefficient. The highest value of which we have record for platinum is 0.003925, which may be taken as the value for annealed platinum free from all impurities. Although there are few data available for estimating the effect of small amounts of impurities on the freezing point of platinum, the indications are that the amount of impurity present in the platinum used in this work was not great enough to change the freezing point

[14] Trans. A. I. M. M. E., **76**, p. 602; 1928.

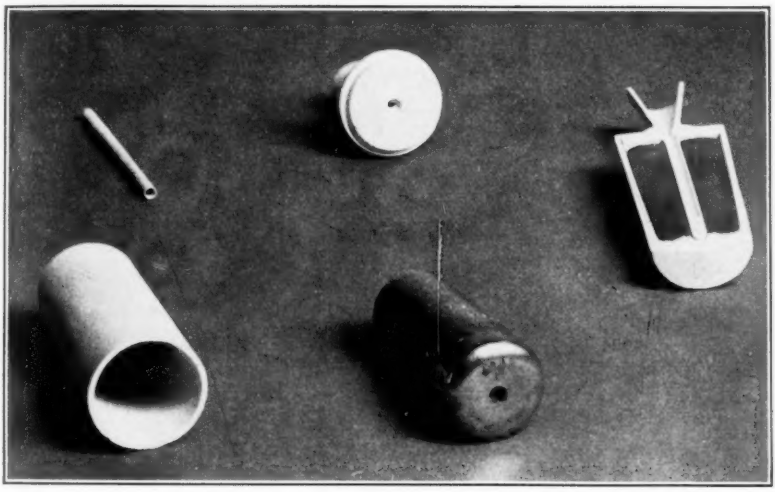

FIGURE 2.—*Photograph of platinum ingot and refractory parts*

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by more than 0.1° or 0.2° C., corresponding to a change in brightness of the standard of less than 0.2 per cent. Any platinum having a temperature coefficient of resistance of 0.00390 or more should serve to reproduce the standard within the limits that can be detected photometrically.

### 3. THE PHOTOMETRIC ARRANGEMENT

The substitution method of photometry was employed, the general arrangement of the apparatus being shown schematically in Figure 3. This is a horizontal plan view excepting that the black body furnace, $F$, and the 45° total reflecting prism above it are shown rotated from their true position through an angle of 90° about the dotted line. Light from the opening in the black body at $F$ passes vertically upward, is turned through an angle of 90° by the prism and passes horizontally through the lens $L$ and the diaphragm $K$. The diaphragm was chromium plated and then blackened. The lens $L$ forms an image of the opening in the black body upon the reflecting test plate $H$ of magnesium carbonate. $N$ is a transmitting test plate

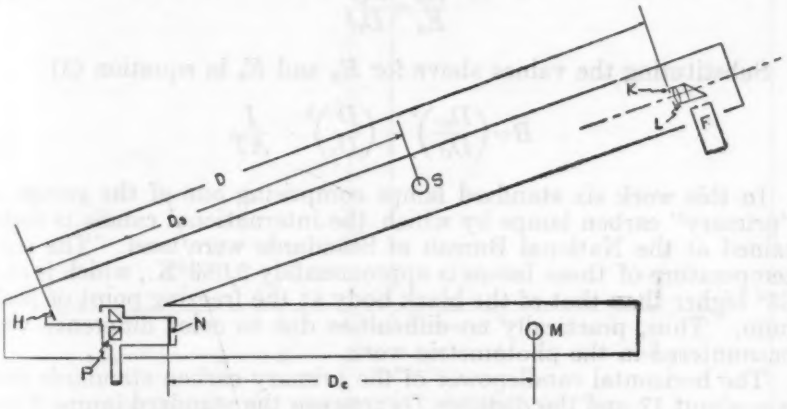


FIGURE 3.—*Plan diagram of the photometer and track*

illuminated by light from a comparison lamp $M$. The apparent brightnesses of these two test plates as seen in the Lummer-Brodhun photometer head at $P$ are adjusted to equality by moving the comparison source.

The optical principle employed is that the illumination of an image produced by an optical system is equal to the product of the brightness of the object and the solid angle of the cone of rays illuminating the image multiplied by the transmission of the optical system.

The illumination $E_B$ on the test plate $H$ due to the image of the black-body opening is given by the formula,

$$E_B = \frac{BAT}{D^2} \tag{1}$$

where

$B$ = the brightness of the black body in candles per square centimeters.

$A$ = the area in square centimeters of the opening in diaphragm $K$.

$T$ = the transmission of the lens and prism.

and

$D$ = the distance in centimeters between the diaphragm $K$ and the test plate $H$.

The illumination $E_S$ on the test plate $H$ due to the light incident on it from the standard lamp $S$ is given by the formula

$$E_S = \frac{I}{D_S^2} \tag{2}$$

where

$I$ = the candle power of the standard lamp $S$.

and

$D_S$ = the distance between the standard lamp $S$ and the test plate $H$.

If the distance between the comparison lamp $M$ and the transmitting test plate $N$ is $D_C$ when a photometric balance is obtained with illumination $E_B$ on the test plate $H$, and $D_{C'}$, when a photometric balance is obtained with illumination $E_S$ on test plate $H$, then

$$\frac{E_B}{E_S} = \frac{D_{C'}^2}{D_C^2} \tag{3}$$

Substituting the values above for $E_B$ and $E_S$ in equation (3)

$$B = \left(\frac{D_{C'}}{D_C}\right)^2 \cdot \left(\frac{D}{D_S}\right)^2 \cdot \frac{I}{AT} \tag{4}$$

In this work six standard lamps comprising one of the groups of "primary" carbon lamps by which the international candle is maintained at the National Bureau of Standards were used. The color temperature of these lamps is approximately 2,080°K., which is only 35° higher than that of the black body at the freezing point of platinum. Thus, practically no difficulties due to color difference were encountered in the photometric work.

The horizontal candlepower of the primary carbon standards used was about 17 and the distance $D_S$ between the standard lamps $S$ and test plate $H$ was about 125 cm, resulting in an illumination on the test plate of approximately 11 m candles. By suitably choosing the distance $D$ and the size of the opening in the diaphragm $K$, approximately the same illumination was obtained when light from the black body during the freezing of the platinum was incident on the test plate. Thus, all photometric measurements that are used to calculate the black body brightness were made with the same photometer field brightness. Also, the distances $D_C$ and $D_{C'}$ were nearly equal, so that only their difference need be known accurately. The photometric settings from which the ratio $\frac{D_{C'}}{D_C}$ was determined were automatically recorded on a drum chart, thus producing freezing and cooling curves such as the one shown in Figure 4.

### 4. METHOD OF MAKING OBSERVATIONS

As explained before, the metal in the liquid state undergoes a violent stirring action so that the entire mass cools to the freezing point before any part of it begins to solidify. For this reason only the observations taken during freezing were used, although the melts were

usually observed. The melts did not differ materially from the freezes, but were usually not as sharply defined at beginning and end. As shown in Figure 4 undercooling before freezing almost invariably occurred.

The procedure in making a run was as follows: The platinum was heated, and all necessary adjustments made to center the image of the black-body opening upon the test plate. To measure the distances from the test plate to the standard lamps and to the diaphragm a steel bar was next clamped in position along the optical axis of the lens. The bar had three calibrated reference marks, one near each end and one at the location of the socket for the standard lamp *S*. It was over 3 m in length, being some 12 to 15 cm shorter than the distance between the test plate and diaphragm. The bar was adjusted until

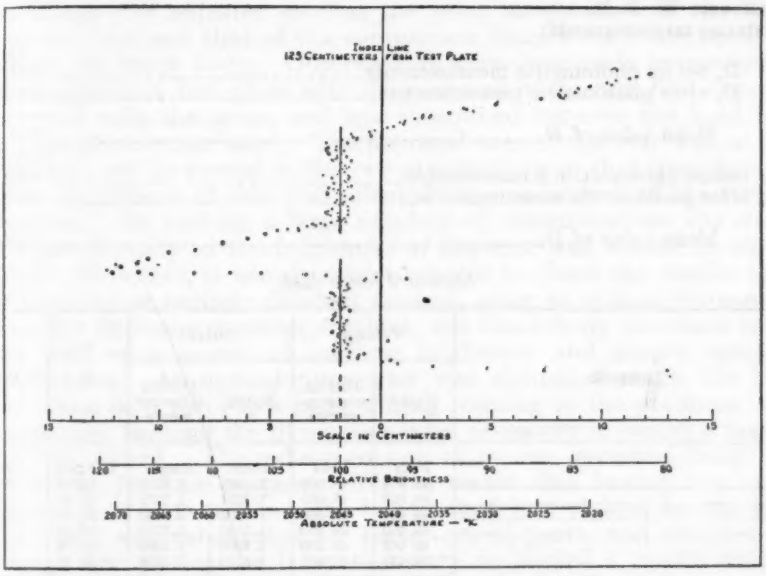


FIGURE 4.—*Automatic record of a typical melt and freeze*

the middle scratch coincided with the center of the lamp socket at *S* and the distances from the diaphragm *K* to one end scratch and from the test plate H to the other end scratch were measured with a short steel scale to within 0.2 mm.

Throughout each run the carbon comparison lamp was maintained at a constant voltage such that its color temperature was approximately midway between that of the black-body standard and that of the standard carbon lamps. The observer made photometric measurements first on three standard lamps, then on three successive freezes of the platinum standard, and finally on three additional standard lamps. Electrical measurements on both the standard and the comparison lamps were made by means of a 5-dial Dieselhorst potentiometer. Following these photometric measurements, the steel bar was again clamped in position on the optical axis and the distance measurements repeated.

The photometric settings made during a run were usually all recorded on a single drum chart. The distances between the average

settings of the comparison lamp for the black-body standard and for the standard lamps were measured by a steel scale to an accuracy of about 0.2 mm.

A sample data sheet is given below. The symbols used have the following meanings:

$D$, the distance between the diaphragm and the test plate.
$D_s$, the distance between the center of the standard lamp socket and the test plate.
$D_c$, the distance between the comparison lamp and the transmitting test plate when a photometric balance is obtained with illumination from the black body in freezing platinum (obtained from drum charts).
$D_c'$, the distance between the comparison lamp and the transmitting test plate when a photometric balance is obtained with illumination from the standard lamp (obtained from drum charts).

Date: October 10, 1929.
Drum charts: 46 and 47.
Observer: W. F. R.
Distance measurements:

| | *cm* |
|---|---|
| D, before photometric measurements | 341. 57 |
| D, after photometric measurements | 341. 60 |
| Mean value of $D$ | 341. 59 |
| $D_s$, before photometric measurements | 125. 74 |
| $D_s$, after photometric measurements | 125. 77 |
| Mean value of $D_s$ | 125. 76 |

*Standard lamp data*

| Lamp No. | Voltage | | Current | | $I$ | $D_s'$ |
|---|---|---|---|---|---|---|
| | Rated | During measurements | Rated | During measurements | | |
| | *Volts* | *Volts* | *Amps.* | *Amps.* | *Candles* | *cm* |
| 44 | 48. 960 | 48. 960 | 1. 3314 | 1. 3316 | 17. 74 | 126. 35 |
| 45 | 48. 960 | 48. 960 | 1. 3291 | 1. 3292 | 17. 49 | 126. 69 |
| 46 | 49. 460 | 49. 460 | 1. 3203 | 1. 3218 | 17. 58 | 126. 55 |
| 49 | 49. 460 | 49. 460 | 1. 3292 | 1. 3292 | 17. 76 | 126. 20 |
| 50 | 49. 460 | 49. 460 | 1. 3269 | 1. 3269 | 17. 64 | 126. 20 |
| 64 | 50. 459 | 50. 459 | 1. 3320 | 1. 3322 | 18. 13 | 125. 15 |
| Mean | | | | | 17. 723 | 126. 19 |

*Data on platinum freezes*

| Freeze No. | $D_c$ |
|---|---|
| | *cm* |
| 1 | 126. 69 |
| 2 | 126. 99 |
| 3 | 126. 88 |
| Mean | 126. 85 |

$A$, area of opening in diaphragm ..... $cm^2$ .. 2. 8598
$T$, transmission of lens and prism ..... per cent .. 76. 93

The brightness of the black body immersed in freezing platinum, computed from the equation (see equation (4), p. 1110)

$$B=\left(\frac{Dc'}{Dc}\right)^2\left(\frac{D}{D_s}\right)^2\frac{I}{AT}$$

is $B=58.82$ candles/$cm^2$.

The diameter of the opening in the diaphragm $K$ was measured both with a microscope comparator by the length measurements section of the National Bureau of Standards and with gages by the gage section. The opening was found to be very slightly out of round, and this fact was taken into account in calculating the area.

The measurement of the combined transmission of the lens and prism, which enters in the result to the first order, and which proved to be somewhat of a problem, was made by two independent methods. In the first, termed the box method, a rectangular light box was constructed, the front of which contained a circular opening through which the rear wall could be viewed. The inside walls were coated with the fumes from burning magnesium ribbon, and several incandescent lamps were placed inside the box and screened so as to illuminate the rear wall as uniformly as possible. The voltage of the lamps was adjusted so that the color temperature of the light from the box and that of the comparison lamp were made equal to that of the black body. Observations were then made by matching the comparison test plate with the rear wall of the box, first directly and next with the prism and lens interposed between the light box and the photometer head. The identical area of the rear wall of the box could not be viewed in the two observations so that irregularities in the brightness of this wall affected the consistency of the results obtained. By making a large number of determinations the effect of nonuniformity of the brightness of the rear wall should be eliminated. However, it was deemed advisable to check the results thus obtained by an entirely different method, using an optical pyrometer.

In the optical-pyrometer method, the black-body standard itself was used as a source of uniform brightness and proper spectral distribution. An optical pyrometer was sighted through the lens and prism into the black body during freezing of the platinum and the current through the pyrometer lamp necessary to secure a match was determined. The red screen was, of course, removed from the pyrometer for this purpose. Next a sector disk having the same transmission as that which the box method had yielded for the lens and prism was substituted for these optical parts, and the current through the pyrometer lamp necessary to secure a match during a freeze of the platinum was again determined. Two other sectors were also used, one having a slightly greater and one a slightly smaller transmission than the first in order to determine the relation between the current through the lamp and the transmission in this region. As it happened, the last two sectors were scarcely needed because the current through the lamp in the two cases, when the first sector and when the lens and prism were used, differed by only 1 part in 10,000, corresponding to a difference of 1 part in 2,000 in the transmission.

Each of three observers made 4 sets of observations, representing in all 18 freezes using the first sector and 18 freezes using the lens and prism. The values obtained are listed in Table 2.

TABLE 2.—*Data on transmission of lens and prism*

| Observer | Box method | Optical-pyrometer method |
|---|---|---|
| | *Per cent* | *Per cent* |
| H. T. W. | 76.93 (Average of 12 sets) | 77.03 (Average of 4 sets). |
| W. F. R. | 76.93 do. | 76.93 Do. |
| F. R. C. | 76.89 do. | 76.85 Do. |
| E. G. A. | 76.97 (Average of 6 sets) | |
| Mean | 76.92 | 76.94 |

## IV. RESULTS

During the first few freezes taken on ingot No. 1, a water-cooled diaphragm was used in contact with the prism. The cooling proved too effective, the prism being cooled sufficiently below room temperature to collect a slight film of moisture from the atmosphere. While these results did not differ appreciably from those obtained later, it was decided to discard all results from runs at the conclusion of which any film could be detected. With air cooling instead of water cooling, no further trouble from films was experienced and no results obtained after the change to air cooling have been discarded.

The photometric settings were made by four observers. Observers (H. T. W. and E. G. A.) had considerable previous experience in photometry, and observers (H. T. W., W. F. R., and F. R. C.) had considerable experience in precision optical pyrometry. The results of individual runs obtained are listed in Table 3, each run being the average of observations on three freezes and six primary standard lamps.

TABLE 3.—*Data on black-body brightness*

| Ingot No. 1 | | | | Ingot No. 2 | | | |
|---|---|---|---|---|---|---|---|
| H. T. W. | W. F. R. | F. R. C. | E. G. A. | H. T. W. | W. F. R. | F. R. C. | E. G. A. |
| c/cm² | c/cm² | c/cm² | c/cm² | c/cm² | c/cm² | c/cm² | c/cm² |
| 58.69 | 58.48 | 58.92 | 58.46 | 58.61 | 58.81 | 59.13 | 58.53 |
| 58.87 | 58.54 | 58.56 | 59.10 | 58.88 | 58.86 | 58.97 | 58.95 |
| 59.15 | 58.78 | 59.23 | 58.67 | 58.65 | 58.59 | 58.46 | 58.73 |
| 59.09 | 58.82 | 59.15 | 59.07 | 59.14 | 59.01 | 59.09 | 59.02 |
| [1] 58.95 | 58.66 | 58.96 | 58.83 | 58.82 | 58.82 | 58.91 | 58.81 |
| Mean of ingot No. 1, 58.85 candles per cm². | | | | Mean of ingot No. 2, 58.84 candles per cm². | | | |

[1] Mean values.

## V. DISCUSSION OF ERRORS

The precision attainable in visual photometry is generally considered to be no better than 1 part in 1,000, and it would be very gratifying if one could be assured that the value for the brightness of the Waidner-Burgess standard has been determined to this order of accuracy. The agreement of the results obtained with ingot No. 1 and ingot No. 2, to 1 part in 6,000 may be looked upon as an unusual coincidence. It is believed, however, that the standard as used in this work is reproducible in any suitably equipped laboratory to within 1 part in 1,000.

The uncertainty in the value obtained for the brightness, due to errors in the measurement of the opening in the limiting diaphragm used is too small to affect the result by more than 0.03 per cent. The distance measurements were all made with sufficient accuracy to make the resultant error negligible, about 0.02 per cent. The measurement of the transmission of the lens and prism, made by two independent measurements each of which is probably good to nearly 0.1 per cent, is considered good to 0.1 per cent. The value for the candlepower of the carbon lamps used is taken to be exact, our result being expressed relative to the candlepower of this group of six lamps. The various errors may be summarized as shown in Table 5.

TABLE 5.—*Summary of possible errors due to various causes*

| | Per cent |
|---|---|
| Area of diaphragm | ±0.03 |
| Distance measurements | ±.02 |
| Transmission of lens and prism | ±.1 |
| Photometric matching | ±.1 |
| Lack of black-body conditions and temperature drop in wall of sight tube | —.2 |
| Sum | +0.25 to —0.45 |

The errors listed in Table 5 are all independent of each other and are not likely to be all of the same sign. The numerical value for the brightness in terms of the group of six lamps used in the measurements is, therefore, probably not high by more than 0.15 per cent nor low by more than 0.35 per cent.

## VI. COMPARISON OF RESULTS WITH THOSE OF OTHER OBSERVERS

The values for the brightness of a black body at the platinum point obtained by Ives, by Brodhun and Hoffmann, and in the present work are given below in terms of the international candle as maintained at the National Bureau of Standards.

| | c/cm² |
|---|---|
| $B_1$ (Ives) | 55.40±0.11 |
| $B_2$ (B. & H.) | 58.26± .15 |
| $B_3$ (W., R., B. & C.) | 58.84+ .20 or −0.09 |

It is obvious that the differences in the values given above can not be due to errors in the photometric comparisons, and are likewise somewhat too large to be entirely accounted for by differences in photometric units. It would seem more logical to conclude that the sources actually differed in intrinsic brightness in the manner indicated by the measurements. It so happens that positive evidence on this point is available.

The freezing point of platinum has been determined, as described elsewhere in this journal [15] by making observations with an optical pyrometer on the same black bodies for which the brightness was determined in this investigation as having the value $B_3$ above. The temperature obtained was 1,773.5° C. Int. Likewise the melting point of platinum was determined by Hoffmann [16] using the experimental arrangement with which the value of brightness cited as $B_2$ was found. The value obtained, 1,771° C., on the basis of $C_2=1.430$ cm deg.,

[15] B. S. Journ. of Research, 6, p. —; 1931.

[16] Zeits. f. Phys., 27, p. 285, 1924.

becomes 1,769.5° C. when reduced to the International Temperature Scale.

Ives made no temperature measurements, but shortly after the publication of this work measurements [17] were made at the National Bureau of Standards with an optical pyrometer on the radiation from small holes in platinum tubes 1 mm in diameter and having walls 0.1 mm thick. The temperature readings at the instant of melting ranged from 1,760° to 1,766° C. More recently Ribaud and Mohr [18] have made similar measurements and report a value of 1,762° C.

The correlation of the temperature measurements made on tubes with the value found by Ives on tubes of radically different dimensions may be open to question. However, these measurements are the only available ones made under even approximately similar conditions. Nevertheless, there can be no doubt that the radiation from such tubes at the time of failure is equivalent to that from a black body at a temperature considerably below the platinum point.

The conditions in the work of Brodhun and Hoffmann were such that the temperature of the black body used may have been either above or below the temperature of the melting platinum. The evidence, both in the case of the brightness measurements and in the case of the temperature measurements, is that the black body used by Brodhun and Hoffmann emitted less radiation than the immersed black body used in the present work, which in turn could not possibly be at a temperature above that of the freezing platinum in which it was immersed.

On the basis that the equivalent temperature and brightness of the three sources used corresponded closely to the observed values, we may calculate the value that each would have obtained with a source at 1,773.5° C.

| Source used | Temperature of source (observed) | Brightness of source (observed) | Brightness calculated for a temperature of 1,773.5° C. |
|---|---|---|---|
| | °C. | c/cm² | c/cm² |
| Platinum tubes | 1,762.5±2 | 55.40±0.11 | 59.10±0.66 |
| Resistance-wound furnace | 1,769.5±2 | 58.26±0.15 | 59.64±0.66 |
| Black body immersed in platinum | 1,773.5±1 | 58.84±0.09 | 58.84±0.09 |

Since a change of 1° C. in the temperature of a black body at the platinum point corresponds to a change of almost 0.6 per cent in brightness, the accuracy of the temperature measurements described is not as great correspondingly as the accuracy of the photometric measurements.

## VII. BLACK-BODY STANDARDS OF HIGHER COLOR TEMPERATURES

The choice of the type of lamp for use in maintaining the value of the international candle was made before the advent of incandescent lamps of higher luminous efficiencies than those with carbon filaments. To-day the carbon lamp has passed almost completely from general

[17] Unpublished work by C. O. Fairchild and H. T. Wensel; September–October, 1924.
[18] C. R., 192, p. 37; 1931.

use. The question naturally arises whether a black body at the color temperature of tungsten lamps, either vacuum or gas-filled, would be a more logical standard than the platinum black body to replace the present carbon lamps as the photometric standard.

In practice, the several national laboratories maintain as working standards vacuum tungsten and gas-filled tungsten lamps, which have been calibrated in terms of the primary carbon standards by various methods. Unfortunately, the national laboratories are not in agreement on the results obtained in such calibrations, so that although they agree approximately on the unit of light as maintained by carbon standards, they do not agree on the unit as represented by derived tungsten standards. Intercomparisons indicate that the discrepancies may amount to as much as 5 per cent. Such a condition may be remedied in one of two ways. The several laboratories may agree on a procedure which will give consistant results in comparing lamps differing in color temperature or a black body at a higher color temperature may be arbitrarily set up as a standard and the unit so defined maintained by tungsten lamps. The objections against defining a new unit are the same as those against any dual standard. Moreover, since the tungsten-filament incandescent lamps in use to-day range in color temperature from about 2,400° to 3,300° K., no one standard will serve for all such lamps until a solution is found for the problem of comparing two lamps differing in color temperature by hundreds of degrees. A cooperative investigation is now being carried on among the national laboratories in which it is hoped the spectral transmission values of several blue filters will be agreed upon. With the use of these filters, the step from one color temperature to another can be made without the difficulties inherent in heterochromatic photometry. The solution of this problem will make the position in the color-temperature scale of the source chosen as the primary standard a matter of secondary importance.

## VIII. SUMMARY

The proposal of Waidner and Burgess for a reproducible standard of light has been experimentally realized. The light emitted by a hollow inclosure of fused thorium oxide immersed in freezing platinum has been found to be reproducible within the limits that can be detected by visual photometry. The brightness of this source was determined as $58.84 \pm 0.09$ candles per square centimeter.

The brightness of a black body at the platinum point probably lies between 58.75 and 59.04 candles per square centimeter.

## IX. ACKNOWLEDGMENTS

Grateful acknowledgment is made to the many sections of the bureau who contributed assistance in this work. In particular the authors wish to express their appreciation to L. R. Kleinschmidt and H. A. Buchheit for preparation of the platinum sponge; to W. H. Swanger and J. S. Acken for melting the sponge into ingots; to E. Wichers for the chemical analysis; to W. F. Meggers and B. F. Scribner for the spectrographic analyses; and to E. G. Anderson who served as one of the four observers.

WASHINGTON, March 5, 1931.

# THE FREEZING POINT OF PLATINUM

By Wm. F. Roeser, F. P. Caldwell, and H. T. Wensel

ABSTRACT

In determining the freezing point of platinum on the International Temperature Scale, measurements were made of the ratio of brightness of black bodies maintained at the freezing points of gold and platinum. The black bodies used were hollow inclosures of fused thorium oxide immersed in the molten metals. Observations were made during the freezing of the metals. Two optical pyrometers were used and observations were obtained on two separate lots of pure platinum by three observers. The metals were heated in air using a high frequency induction furnace to secure automatic stirring of the freezing metals and to avoid contamination from furnace windings.

The freezing point was found to be 1,773.5° C.

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## I. INTRODUCTION

Since the International Temperature Scale [1] adopted in 1927 by the General Conference on Weights and Measures defines temperatures above the freezing point of gold by means of Wien's law of radiation, any determination of the melting or freezing point of platinum on this scale must be based upon measurements of the radiation emitted at some known wave length from a black body maintained at the temperature in question.

There are a number of methods by which a black body may be brought to or maintained at the melting or freezing point of a metal. Worthing [2] has used hollow cylinders of the metal carrying an electric current controlled so as to bring the metal slowly up to the melting point. Observations may then be made on the radiation emitted from a small opening in the side of the cylinder at the instant of melting. Mendenhall [3] has used a strip of the metal folded into a hollow wedge, the angle of the wedge being so small that the radiation from the inside of the wedge approximated that from a black body. Such methods are, in some cases, the only ones available, but where feasible the methods described below are to be preferred.

Another method which has been much used is to heat a furnace to such a temperature that a small bit of the metal located in the

[1] G. K. Burgess, B. S. Jour. Research, **1**, p. 635, October, 1928.
[2] A. G. Worthing, Phy. Rev. N. S., **10**, p. 377; 1917.
[3] C. E. Mendenhall, Astrophy. J., **33**, p. 91; 1911.

furnace will just melt or freeze. The bit of metal, the melting or freezing of which serves to indicate the proper time to make observations, is usually welded between thermocouple elements at the hot junction, melting or freezing being indicated by a constant value of the emf of the thermocouple for a short period of time while the temperature of the furnace is changing slowly. This method, commonly referred to as the wire method, has been studied by Fairchild, Hoover, and Peters,[4] who have discussed its limitations in great detail. The one obvious disadvantage of the wire method is that the melting or freezing metal indicates the temperature of only a very small region of the furnace, whereas the radiation measured depends on the temperature of other parts of the furnace as well. At the temperature of freezing platinum one would be very fortunate if the equivalent temperature of the radiation emitted from the furnace did not differ by several degrees from the temperature of the furnace at the point where the melting sample was located.

A better method, which is termed the crucible method, is to immerse a hollow inclosure in a bath of the metal and to make observations during the time the metal is melting or freezing. Since no considerable temperature differences can exist in such a bath of metal, this method insures that the radiation measured is very nearly that from a black body at the melting or freezing point in question. Freezing points are preferable to melting points, since temperature gradients are likely to be smaller in liquid than in solid metal. If, finally, the freezing is done in a high frequency induction furnace with reduced power on the furnace, the action of the electromagnetic field on the currents induced in the metal produces a violent stirring, and the possibility of appreciable temperature gradients is further reduced.

In spite of the fact that the crucible method appears to be the ideal one for accurate melting or freezing point determinations, it has not been very widely used. For example, no determination of the freezing or melting point of platinum by this method is to be found in the literature. One reason for this is probably the fact that the crucible method demands refractories from which crucibles may be made which in prolonged contact with the molten metal will produce no appreciable contamination. The freezing points of palladium [5] and nickel [6] have recently been accurately determined in crucibles which produced no perceptible contamination, and the recent development of fused thorium oxide [7] provides a refractory in which pure platinum may be repeatedly melted without detrimental contamination. In view of the importance of the platinum point and the uncertainty felt regarding its temperature, determinations have been made by the crucible method, using crucibles of fused thorium oxide and melting the metal in an induction furnace.

## II. PREVIOUS WORK

Since 1912 two determinations of the melting point of platinum have been reported. In 1924 Hoffmann,[8] using the wire method in an iridium wound furnace, obtained the value 1,771° C. on the scale

[4] Fairchild, Hoover, and Peters, B. S. Jour. Research, **2**, p. 931; May, 1929.
[5] Fairchild, Hoover, and Peters, B. S. Jour. Research, **2**, p. 931; May, 1929.
[6] Wensel and Roeser, B. S. Jour. Research, **5**, p. 1309; December, 1930.
[7] Swanger and Caldwell, B. S. Jour. Research, —, p. —, 1931.
[8] Fr. Hoffmann, Zeits. f. Phys., **27**, p. 285; 1924.

then in use at the Physikalisch-Technische Reichsanstalt, based on 1,063° C. for the melting point of gold and a value of 1.430 cm degrees for $C_2$. This value reduces to 1,769.5° C. on the present International Temperature Scale based on $C_2 = 1.432$ cm degrees. Since the completion of the work described in this paper Ribaud and Mohr [9] reported measurements on tubes of platinum, such as were used by Worthing in the case of tungsten, and obtained a value of 1,762° C. Int.

Reviewing the literature, we find 14 independent determinations of the melting point of platinum. Nine of these, listed in Table 1, were made by employing uncertain extrapolation methods and although they were of value at the time they were made, they are now considered to be of historical interest only. The remaining five, including the two recent determinations noted above, are listed in Table 2. These five determinations were made by measuring with an optical pyrometer the ratio of brightness of black bodies at the melting points of gold and platinum, respectively, and calculating the platinum point by means of Wien's law of radiation.

TABLE 1.—*Determinations of the melting point of platinum by extrapolation methods*

| Observers | Date | Property extrapolated | Reported value | Corrected value on present scale |
|---|---|---|---|---|
| | *Year* | | *° C.* | *° C.* |
| Violle [1] | 1877 | Specific heat | 1,779 | |
| Barus [2] | 1892 | Electomotive force | 1,855 | |
| Holborn and Wien [3] | 1892 | do | 1,780 | |
| Harker [4] | 1905 | do | 1,710 | |
| Holborn and Henning [5] | 1905 | do | 1,710 | |
| Do.[5] | 1905 | Spectral emissivity | 1,729 | 1,739 |
| Waidner and Burgess [6] | 1907 | Electromotive force | 1,731 | |
| Do.[6] | 1907 | Spectral emissivity | 1,750 | 1,761 |
| Day and Sosman [7] | 1912 | Electromotive force | 1,752 | |
| Mean | | | 1,755 | |

[1] Violle, Comp. Rend., **85**, p. 543; 1877.
[2] Barus, Bull., **54**, U. S. Geological Survey; 1889. Die Physikalische Behandlung und die messung hoher Temperaturen, Leipzig; 1892.
[3] Holborn and Wien, Wied, Ann., **47**, p. 107; 1892.
[4] Harker, Royal Society, A., **76**, 1905.
[5] Holborn and Henning, Sitz. Ber. d. Koen Preuss. Akad. Wis., p. 311; 1905.
[6] Waidner and Burgess, B. S. Bull., **3**, p. 163; 1907.
[7] Day and Sosman, Am. J. Sci., **33**, p. 517; 1912.

TABLE 2.—*Determinations of the melting point of platinum with optical pyrometer by the ratio of brightness method*

| Observers | Date | Scale used | | Value reported | Value on the International Temperature Scale |
|---|---|---|---|---|---|
| | | $C_2$ | Au point | | |
| | *Year* | *cm deg.* | *° C.* | *° C.* | *° C.* |
| Nernst and Von Wartenburg [1] | 1906 | 1.46 | 1,064 | 1,745 | 1,763 |
| Holborn and Valentiner [2] | 1907 | 1.42 | 1,064 | 1,789 | 1,777 |
| Waidner and Burgess [3] | 1907 | 1.45 | 1,064 | 1,753 | 1,764 |
| Hoffmann [4] | 1924 | 1.430 | 1,063 | 1,771 | 1,769.5 |
| Ribaud and Mohr [8] | 1931 | 1.432 | 1,063 | 1,762 | 1,762 |
| Authors | 1931 | 1.432 | 1,063 | 1,773.5 | 1,773.5 |

[1] Nernst and Von Wartenberg, Verh. d. Deut. Phys. Ges. p. 48; 1906.
[2] Holborn and Valentiner, Ann. d. Phys., (4) **22**, p. 1; 1907.
[3] Waidner and Burgess, B. S. Bull., **3**, p. 163; 1907.
[4] Fr. Hoffmann, Zeits. f. Phys., **27**, p. 285; 1924.
[8] G. Ribaud and P. Mohr., Comp. Rend., **192**, p. 37; 1931.

[9] G. Ribaud and P. Mohr, Comp. Rend., **192**, p. 37; 1931.

## III. PRESENT WORK

### 1. TEMPERATURE SCALE USED AND COMPUTATION METHODS

On the International Temperature Scale adopted in 1927, the temperature $t$, in °$C$., of a black body above the freezing point of gold (1,063° $C$. or 1,336° $K$.) is defined by the formula:

$$\log_e R = \log_e \frac{J}{J_1} = \frac{1.432}{\lambda}\left(\frac{1}{1{,}336} - \frac{1}{t+273}\right) \quad (1)$$

(where)

$$J_1 = C_1\lambda^{-5}e^{-\frac{C_2}{\lambda 1{,}336}} \quad (2)$$

$$J = C_1\lambda^{-5}e^{-\frac{C_2}{\lambda(t+273)}} \quad \text{(Wien's law)} \quad (3)$$

and $C_2 = 1.432$ cm deg.

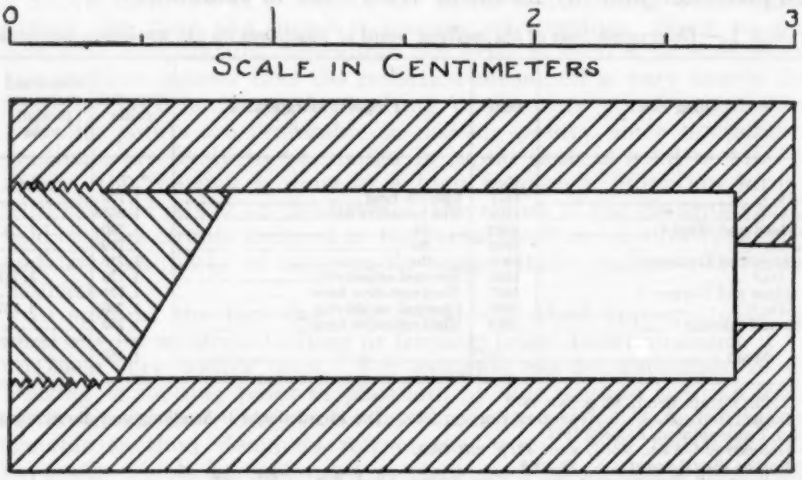


FIGURE 1—*Platinum black body used in calibrating optical pyrometers*

The brightness ratio $\frac{J}{J_1}$ for the platinum point, using red light, is approximately 300, and consequently a sector disk of about 1° angular opening would be required to measure this ratio in one step. The uncertainty in the measurement of such an opening would be about 20 seconds of arc corresponding to an uncertainty of nearly 1° in the computed temperature. The use of sector disks of larger openings to measure the ratio in two steps very materially reduces the uncertainty due to the errors of measurement of the angular opening. For example, two of the sectors, No. 3 and No. 2, used in this work transmit, respectively 0.7611 and 2.6258 per cent of light, an uncertainty of 20 seconds in the measurement of the angular opening corresponding to only 0.4° and 0.1°C., respectively.

In measuring the ratio of brightness in two steps, the hollow platinum cylinder shown in Figure 1 was used to obtain measurements at intermediate temperatures. The cylinder was inclosed to prevent

air currents produced by the rotating sector disk from causing fluctuations in the temperature of the cylinder. The inclosed space was evacuated to prevent overheating of the glass window. The thick walls and the form of the platinum cylinder insure a fairly high degree of temperature uniformity inside the cylinder and by the use of storage batteries for supplying power to the furnace, the temperature could be maintained very nearly constant.

The procedure followed in taking observations and the methods of computing the freezing point of the platinum will appear from the following examples. The value given in (*b*) of each example was obtained by observer W. F. R. as the mean of all observations with this pyrometer, sector, and ingot. All other values given in these examples are the means for the three observers. The mean for the three observers at the gold point and at the intermediate temperatures were used throughout, since the variations among the values by the various observers were equivalent to not more than 0.3°C.

The first example is for pyrometer lamp F10 when using sector No. 2 (transmission 2.6258 per cent).

(*a*) The telescope was sighted into the black body immersed in freezing gold and the lamp current required to obtain a brightness match was found to be 0.11680 ampere. (No sector used.)

(*b*) The telescope was sighted through sector No. 2 into the black body immersed in freezing platinum and the lamp current required to obtain a brightness match was now found to be 0.14944 ampere.

(*c*) The telescope was sighted through a sector disk of 13.013 per cent transmission into the black body shown in Figure 1, the temperature of which was adjusted so that a match was obtained when the current through the lamp was 0.11680 ampere.

(*d*) With the temperature of the black body maintained constant at the same temperature as in (*c*), the sector was removed and the lamp current now required to obtain a match was found to be 0.14911 ampere.

(*e*) Substituting in the equation (1) defining the temperature scale:

$$\frac{1}{0.13013} \text{ for } \frac{J}{J_1}$$

and $0.6537\times10^{-4}$ cm for $\lambda$, the effective wave length for the temperature interval in question, the temperature of the black body was found to be 1,252.8° C.

(*f*) From the temperature 1,252.8° C. for 0.14911 ampere and the corresponding value of $\frac{di}{dt}$ for lamp F10, we find that 0.14944 ampere corresponds to 1,254.6° C.

(*g*) The equation:

$$\log_e \frac{J}{J_m}=\frac{1.432}{\lambda'}\left(\frac{1}{1{,}254.6+273}-\frac{1}{t+273}\right) \qquad (4)$$

similar to equation (1), may be derived from Wien's law and upon substituting for $\frac{J}{J_m}$, $\frac{1}{0.026258}$, and for $\lambda'$, $0.65226\times10^{-4}$ cm, the effective wave length of the red screen for the temperature interval used here, we obtain 1,772.6° C. for the freezing point of platinum from this particular set of observations.

The next example is for pyrometer lamp F10 when using sector disk No. 3. (Transmission 0.7611 per cent.)

(*a*) The current required to obtain a brightness match at the freezing point of gold was 0.11680 ampere as before.

(*b*) The telescope was sighted through sector disk No. 3 into the black body immersed in freezing platinum, and the current required to obtain a brightness match was found to be 0.12781 ampere.

(*c*) By using sector disks with various openings, the current-temperature relation of the lamp was determined by the method employed in (*c*), (*d*), and (*e*) of the first example.

(*d*) From this relation, we find that the current of 0.12781 ampere corresponds to a temperature of 1,133.5° C.

(*e*) Using the equation:

$$\log_e \frac{J}{J_m} = \frac{1.432}{\lambda''}\left(\frac{1}{1{,}133.5+273} - \frac{1}{t+273}\right) \quad (5)$$

also similar to equation (1), and substituting $\frac{1}{0.007611}$ for $\frac{J}{J_m}$ and for $\lambda''$, $0.65262\times10^{-4}$ cm, the effective wave length of the red screen for the temperature interval used here, we obtain 1,773.4° C. for the freezing point of platinum from this set of observations.

The mean effective wave length, $\lambda$, of the red glass screen for a given temperature interval $\theta_1$ to $\theta_2$ is that wave length at which the ratio of black body radiation intensities at the two temperatures is equal to the ratio of the brightness of a black body at $\theta_1$ to that of a black body at $\theta_2$, both viewed through the red screen. The values of $\lambda$ were computed from the spectral transmission of the red glass filter and the average observer's visibility curve as described by Fairchild, Hoover, and Peters.[10] Characteristics of the red glass screen are given in that paper.

All the sector disks used had two openings and were made by mounting steel strips on aluminum disks. The edges of the steel strips were ground or "lapped" straight and aligned to be radial with the aid of a circular dividing engine.

## 2. EXPERIMENTAL PROCEDURE

The observations on the freezing point of platinum were made upon the same crucibles of platinum as were used in the work on "The Waidner-Burgess Standard of Light" [11] reported elsewhere in this journal. The platinum (approximately 185 g) containing the immersed black body is shown in Figure 2. The sight tube or immersed black body, and the crucible were of a very pure grade of fused thorium oxide as described elsewhere [12] in this journal. The crucibles and sight tubes used with both the platinum and the gold were identical in all respects. The metals were both melted in air, by means of a high-frequency induction furnace. There are several advantages to be gained by the use of this type of furnace, the important ones being the stirring of the molten metal mentioned earlier and the freedom from contamination such as might occur from the metallic vapors from the winding in a resistance type of electric furnace. Cracking of the crucible caused no trouble, since the molten metal will not flow through narrow cracks in the crucible unless heated greatly above the melting point.

Two separate lots of platinum designated as ingot No. 1 and ingot No. 2 prepared at this bureau especially for this purpose, and two lots of gold, the purest obtainable from the Bureau of the Mint, were used. The tests made of the purity of the platinum are described elsewhere [13] and indicate that the degree of contamination was

[10] See footnote 4, p. 1120.
[11] Wensel, Roeser, Barbrow, and Caldwell, B. S. Jour. Research, **6**, p. 1103; 1931.
[12] Swanger and Caldwell, B. S. Jour. Research, **6**, p. 1131; 1931.
[13] Wensel, Roeser, Barbrow, and Caldwell, B. S. Jour. Research, **6**, p. 1103; 1931.

scarcely great enough to affect the freezing point by more than 0.2° C. It is estimated that the total impurities were always less than 0.003 per cent during the course of this work.

Two optical pyrometers were used, each provided with a lamp having optically flat windows. The first of these pyrometers, shown in Figure 3, has been described by Fairchild and Hoover.[14] The

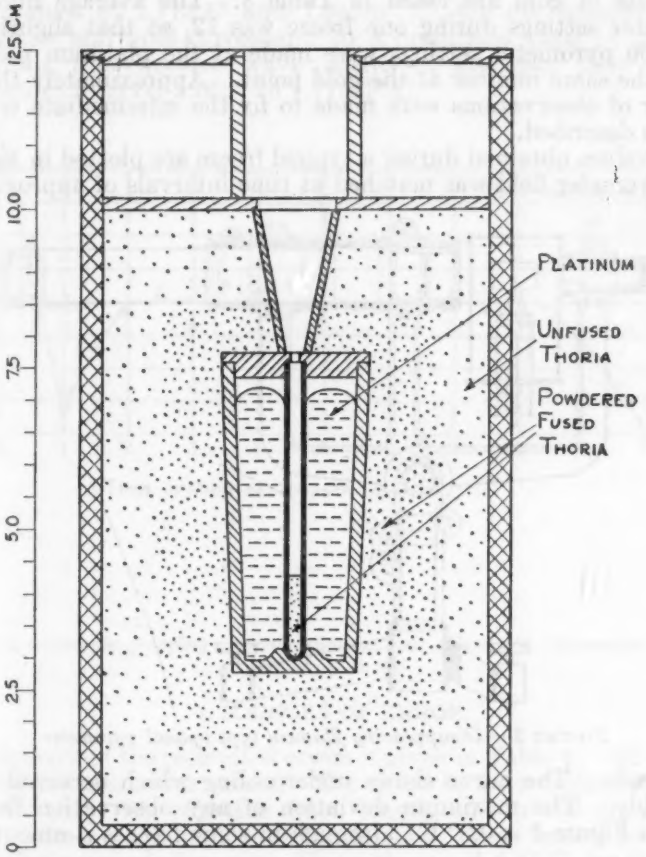


FIGURE 2.—*Cross-section showing platinum, sight tube, crucible, and insulation*

other pyrometer similar to the first, but giving a much higher magnification, was designed for use as a micropyrometer. The precision attainable with this pyrometer containing lamp F15, was slightly less than that attainable with the first, containing lamp F10, but the mean of the series of values obtained with it was nevertheless given the same weight as each of the two series obtained with the other pyrometer.

The telescopes were equipped with 45° total reflecting prims so that the telescopes were horizontal while the crucibles were vertical.

[14] Fairchild and Hoover, J. Opt. Soc. Am. and Rev. Sci. Insts., **7**, No. 7, p. 543; 1923.

### 3. RESULTS

All three of the authors served as observers. A value for the freezing point was calculated from the results of each observer using each sector disk with each lamp on each lot of platinum, excepting that lamp F15 was not used on the first lot of platinum, ingot No. 1. The 18 values thus obtained, representing 43 freezes of platinum and 47 freezes of gold are listed in Table 3. The average number of pyrometer settings during one freeze was 12, so that slightly more than 500 pyrometer settings were made at the platinum point and about the same number at the gold point. Approximately the same number of observations were made to fix the intermediate temperatures as described.

The values obtained during a typical freeze are plotted in Figure 4. The pryometer field was matched at time intervals of approximately

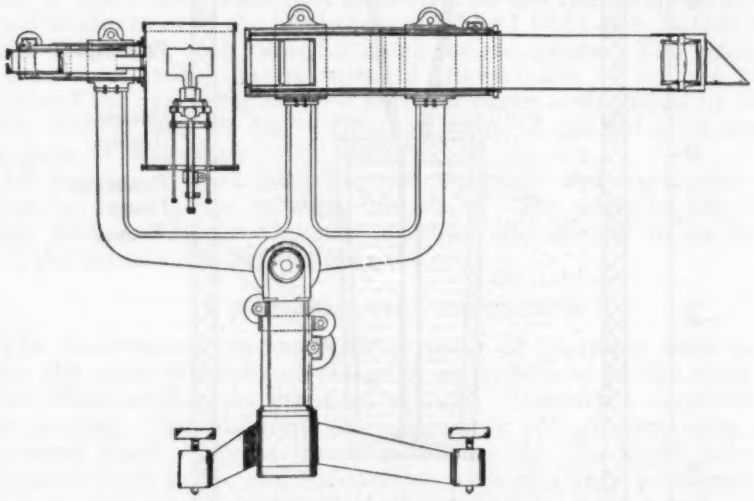

FIGURE 3.—*Disappearing filament type optical pyrometer*

30 seconds. The curve shows undercooling which occurred almost invariably. The maximum deviation of any observation from the mean in Figure 4 is 0.8° C., although in some freezes it amounted to 1.0° C.

TABLE 3.—*Summary of determinations of the freezing point of platinum*

| Observer | Ingot No. 1 lamp F10 | | Ingot No. 2 lamp F10 | | Ingot No. 2 lamp F15 | | Mean for observer |
|---|---|---|---|---|---|---|---|
| | Sector No. 2 | Sector No. 3 | Sector No. 2 | Sector No. 3 | Sector No. 2 | Sector No. 3 | |
| | °C. | °C. | °C. | °C. | °C. | °C. | °C. |
| H. T. W. | 1,773.7 | 1,774.0 | 1,773.0 | 1,773.7 | 1,774.0 | 1,775.8 | 1,774.0 |
| W. F. R. | 1,774.1 | 1,773.7 | 1,772.6 | 1,773.4 | 1,773.6 | 1,775.3 | 1,773.8 |
| F. R. C. | 1,772.1 | 1,771.9 | 1,771.9 | 1,773.3 | 1,773.2 | 1,774.0 | 1,772.7 |
| Mean | 1,773.3 | 1,773.2 | 1,772.5 | 1,773.5 | 1,773.6 | 1,775.0 | 1,773.5 |
| Mean | 1,773.2 | | 1,773.0 | | 1,774.3 | | |
| Mean | F. P.=1,773.5° C. Int. | | | | | | |

The observations on the crucible of gold taken throughout the work indicated that any change which took place in the pyrometer lamps corresponded to not over 0.1° C., the limit that can be detected with the pyrometers used. After the observations on the platinum were completed, a new crucible of gold was made up and observations with each lamp on the second crucible differed by less than 0.1° C., from those on the first crucible.

The values of 1,773.5° and 1,063.0° C., for the freezing points of platinum and gold correspond to a brightness ratio of 299.0 for $\lambda = 0.6528\mu$, the effective wave length of the color filter for the temperature interval 1,063° to 1,773.5° C.

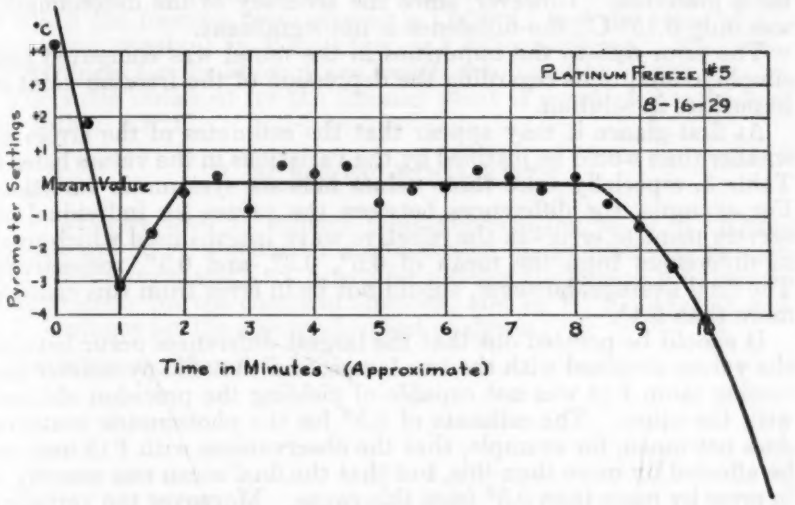


FIGURE 4.—*Sample freezing curve, showing variations of pyrometer settings about the mean*

## 4. SOURCES OF ERROR

A summary of the estimated errors is given in Table 4. All of these estimates are maximum values. The errors in the transmission of the sector disks, in the effective wave length, and in the photometric matching are not difficult to estimate, since these factors have been studied for a period of years. The estimate of 0.3° C. for the maxi-

TABLE 4.—*Summary of estimated errors*

| Source of error | Equivalent in degrees | |
|---|---|---|
| | Sector No. 2 | Sector No. 3 |
| Transmission of sector | 0.1 | 0.4 |
| Effective wave length | .4 | .4 |
| Photometric matching | .5 | .5 |
| Temperature gradients and lack of black body conditions | .3 | .3 |
| Impurity of metal | .2 | .2 |
| Maximum error if all are of same sign | 1.5 | 1.8 |

mum error due to the lack of black body conditions and temperature gradients in the walls of the sight tube is based upon measurements made at the freezing point of gold using thorium oxide and graphite black bodies. A hollow inclosure of graphite immersed in a freezing metal may be taken as a 100 per cent black body for this purpose and the temperature drop through the wall may be neglected, since the thermal conductivity of graphite is known to be high. The measurements indicated that the brightness of the thorium oxide black body was higher than that of the graphite black body by an amount equivalent to 0.1° C. This difference is opposite in sign to the difference that one deduces from a consideration of the physical properties of these materials. However, since the accuracy of the determination was only 0.15° C., the difference is not significant.

The error due to the impurities in the metal was computed from simple assumptions regarding the depression of the freezing point by impurities in solution.

At first glance it may appear that the estimates of the errors are smaller than would be justified by the variations in the values listed in Table 3, especially since these values indicate systematic variations. For example, the differences between the values for individual observers point to errors in the effective wave lengths used which result in differences from the mean of 0.5°, 0.3°, and 0.8°, respectively. The final average, however, should not be in error from this cause by more than 0.4°.

It should be pointed out that the largest differences occur between the values obtained with the two lamps, and that the pyrometer containing lamp F15 was not capable of yielding the precision obtained with the other. The estimate of 0.5° for the photometric matching does not mean, for example, that the observations with F15 may not be affected by more than this, but that the final mean can scarcely be in error by more than 0.5° from this cause. Moreover the variations in Table 3 are not all due to one cause. A different red screen was used with the two pyrometer lamps, requiring an independent determination of the spectral transmission from which to compute the effective wave length to be used.

While the less precise observations with lamp F15 have apparently been given equal weight with those taken with lamp F10, this is really not the case. Of the 43 freezes taken, 30 were obtained with ingot No. 2. Of these 30 freezes, 12 were obtained with F10 and 18 with F15, but these 18 have been given equal weight with the 12 with F10. Moreover, since two-thirds of the values in Table 3 were obtained with lamp F10, the final average is determined largely by the results obtained with the pyrometer of greater precision. On the whole, the agreement between the values obtained with the two pyrometers is all that could be expected under the circumstances, and the final mean does not depend greatly on the method used in averaging the results.

The probable error of the mean, based on the agreement among themselves of the 18 values of Table 3, is 0.15° C. The value obtained for the freezing point, 1,773.5° C. Int., is considered to be accurate to 1°.

## IV. SUMMARY

The freezing point of platinum has been determined on two distinct lots of metal of exceptionally high purity. Measurements were made by three observers using two precision optical pyrometers.

Hollow inclosures of fused thorium oxide were immersed in molten platinum and in molten gold. The metals were melted in air in fused thorium oxide crucibles by means of a high frequency induction furnace. Observations of the relative brightness, at wave length $0.6528\mu$, during the freezing of the metals yielded 1,773.5° C. for the freezing point of platinum on the International Temperature Scale on which the freezing point of gold is 1,063° C. and the value of $C_2$, the second constant in Wien's law, is 1.432 cm degrees. The ratio of brightness for the above wave length was found to be 299.0.

The value obtained for the freezing point is considered to be correct within ±1° C.

## V. ACKNOWLEDGMENTS

The authors wish to express their appreciation to L. R. Kleinschmidt and H. A. Buchheit for preparation of the platinum sponge, to W. H. Swanger and J. S. Acken for melting the sponge into ingots, to E. Wickers for the chemical analyses, and to W. F. Meggers and B. F. Scribner for the spectrochemical analyses.

WASHINGTON, March 4, 1931.

# SPECIAL REFRACTORIES FOR USE AT HIGH TEMPERATURE

By Wm. H. Swanger and Frank R. Caldwell

ABSTRACT

The choice of the most suitable refractory for the laboratory melting of pure metals at temperatures from 1,700° up to 2,200° C. without detrimental contamination of the metal by the refractory depends upon a number of factors, such as the stability of the refractory at the higher temperatures, the means available for forming and firing of crucibles, the type of melting furnace, chemical action of the particular metal in question, etc.

Methods are described in detail for the preparation of crucibles and other shapes from the oxides of thorium, magnesium, zirconium, and beryllium.

Thorium oxide, with a melting point above 3,000° C., is the most refractory of the four oxides named. The method used for fusing this oxide is described. Crucibles made of fused thorium oxide have been used in the determinations of the melting points of platinum and rhodium.

Crucibles of the commercial fused magnesium oxide are not satisfactory for work with metals of the highest purity, but crucibles prepared from the so-called "C. P." or reagent grade of powdered magnesium oxide have been used at temperatures up to 2,000° C. without detrimental effect upon the metal melted.

The commercial electrically fused or sintered zirconium oxide contains small amounts of silica. Crucibles of this material have been used at temperatures up to 2,000° C., but unless the melting is done in air, there is danger of contamination of the metal by the silicon in the refractory.

From a few experiments made with a small amount of the very pure oxide there are indications that, if available commercially, beryllium oxide might be a satisfactory refractory for use at high temperatures.

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## I. INTRODUCTION

An ever-present requirement in working with pure metals is a suitable crucible in which they may be melted without contamination. The choice of the most suitable refractory material for the laboratory melting of pure metals or alloys depends upon factors which are somewhat different from those governing the choice of refractories for commercial melting. For example, the cost of the material is not or-

dinarily of particular importance. The refractory oxides discussed in this paper are considered as research materials, and if they satisfy other requirements made of them their cost is of secondary importance.

Where the maintenance of extreme purity of the metals to be melted is required it is generally more satisfactory or even quite necessary to make the crucibles in the laboratory rather than to attempt to use commercial crucibles. Then the procedures necessary and means available for the fabrication of the required shapes are factors to be considered. The type of furnace, the temperature to which the metal is to be heated, and the effect of the refractory material upon the purity of the metal are important factors in the choice of refractories.

Pure graphite is a very satisfactory refractory material for the melting of metals which do not combine with it. It is one of the most refractory materials and can be purchased in the form of bars or rods from which various shapes can be readily machined. However, the use of graphite is limited from the fact that it combines with many molten metals, and that it oxidizes rapidly at the higher temperatures.

There are available several refractory oxides which are inert to most molten metals, even at the higher temperatures. The results obtained with magnesium oxide, zirconium oxide, and zirconium silicate crucibles for melting pure metals have been reported in a previous publication from this bureau.[1] Additional information that has been secured on these materials since that time, the use of thorium oxide crucibles for melting platinum and other metals of the platinum group, and a few observations on the suitability of beryllium oxide as a refractory material are recorded in the present paper.

These materials are not discussed from a strictly ceramic viewpoint. It is intended merely to describe the methods in use in the National Bureau of Standards laboratories for preparing refractory shapes in which to heat metals or alloys of the highest purity to temperatures up to 2,200° C. without contamination from the refractory.

## II. GENERAL CONSIDERATIONS

The first and most obvious requirement for a crucible is, of course, that it shall not soften or collapse at the temperature at which it is to be used. The melting points of thorium oxide and beryllium oxide have not been exactly determined as yet. Probably the statement that the melting point of thorium oxide is above 3,000° C. and that of beryllium oxide is above 2,400° C. is as close an approximation as can be given at the present time. Kanolt[2] has determined the melting point of magnesium oxide to be 2,800° C. The melting point of zirconium oxide was determined by Washburn and Libman[3] as approximately 2,700° C. Podszus,[4] assigned the value 2,950° to 3,000° C. to it. Washburn[5] also states that the melting point of the mineral zircon (zirconium silicate) is 2,550° C.

The exact melting point of the pure crucible material does not always determine the temperature to which the material in the cru-

[1] Louis Jordan, A. A. Peterson, and L. H. Phelps, Refractories for Melting Pure Metals: Iron, Nickel Platinum, Trans. Am. Electrochem. Soc., **50**, p. 155; 1926.
[2] C. W. Kanolt, Melting Points of Some Refractory Oxides, B. S. Sci. Paper No. 212; 1913.
[3] E. W. Washburn and E. E. Libman, An Approximate Determination of the Melting Point Diagram of the System Zirconia-Silica, J. Am. Ceram. Soc., **3**, p. 634; 1920.
[4] E. Podszus, On the Melting of and Preparation of Crucibles of Zirconium Dioxide, Z. Angew. Chemie, **30**, p. 17–19; 1917.
[5] See footnote 3.

cible may be heated with safety, because so much depends upon the conditions of heating. For example, Kanolt[6] states that magnesium oxide heated under reduced pressure (0.5 to 1.0 cm of Hg) volatilized completely before it melted. When heated at atmospheric pressure in contact with carbon, it volatilizes rapidly at temperatures above 2,000° C. Furthermore, if the metal within the crucible is heated by induction, as in a high-frequency induction furnace, the metal is always hotter than the crucible, while if heated in an electrical-resistance furnace or a fuel-fired furnace where the metal is heated by conduction of heat through the walls of the crucible, the crucible is always at least as hot, if not hotter than the metal inside it. Slight amounts of impurity, such as bonding materials used in forming the crucibles, may lower the softening point of the crucible by as much as several hundred degrees below the melting point of the pure refractory material.

It may be of interest to note the temperatures at which crucibles of these materials have been used successfully at the National Bureau of Standards. Crucibles of zirconium oxide bonded with clay are regularly used for melting platinum and platinum-rhodium alloys containing up to 20 per cent of rhodium in a high-frequency induction furnace. The temperature of the molten metal is always over 1,770° C. The crucibles show no signs of softening. They have also been used for melting rhodium, in which case the temperature attained is at least 2,000° C.

Crucibles of commercial zirconium silicate are not at present in use for melting pure metals because of impurities introduced into the metals from the crucibles. If a purer grade of zircon were available, or where purity of the metal is not of prime importance, crucibles of this material would undoubtedly be useful at temperatures up to 2,000° C.

Magnesium oxide crucibles prepared as described later in this paper have been used at 1,800° C. If not in contact with carbon such crucibles probably could be used at temperatures several hundred degrees higher.

Beryllium oxide, from the results of a very few experiments, appears to be somewhat more resistant than magnesium oxide to reduction by carbon at 2,000° C. and at atmospheric pressure.

Crucibles made of fused thorium oxide have been used to melt a platinum-iridium alloy (73 per cent Ir-27 per cent Pt) whose melting point was determined to be approximately 2,200° C. It is quite probable that crucibles of this material will stand a temperature of 2,500° C. without softening.

In addition to refractoriness, the choice of the type of crucible material may be influenced by the means available for forming or firing the crucible. The refractory may be ground with water to form a "slip" which is then cast into plaster of Paris molds to form crucibles of the desired shapes. This method is not applicable to refractory oxides that hydrate rapidly, such as calcium or magnesium oxides. The method is, moreover, rather wasteful of material.

Another method is to moisten the refractory material with a suitable bonding solution and tamp it into a mold of the required shape. If a variety of shapes are desired it may be convenient to machine

[6] See footnote 2, p. 1132.

molds from graphite. When a number of crucibles of the same shape are required steel molds may be more convenient.

In general, it is desirable that the crucibles be fired beforehand to a temperature higher than that at which they are to be used. The Arsem vacuum furnace and the high-frequency induction furnace have been used to fire crucibles to temperatures in the range 1,700° to 2,000° C. In the latter type of furnace, a hollow cylinder of graphite placed around the refractory crucible within the inductor coil serves as a heater for the crucible.

## III. THORIUM OXIDE

The purest grade of thorium oxide obtainable is used for the work with pure metals. The thorium oxide prepared commercially for the incandescent gas-mantle industry generally contains a small amount of sulphate which should be removed before the material is used to make crucibles in which pure metals are to be melted. Sulphates mixed with refractory oxides will under certain conditions of heating be reduced to sulphides. Experience has shown [7] that metals capable of combining with sulphur will be subject to a sulphur "pick-up" when melted in a refractory oxide crucible that is contaminated with sulphides. Specially prepared thorium oxide is obtainable in a state of purity suitable for the melting of metals of highest purity. The material as purchased requires no treatment other than fusion. The best grades of thorium nitrate obtainable commercially also generally contain a small amount of sulphate, but thorium nitrate, being readily soluble in water, is more easily purified than thorium oxide, and a satisfactory grade of thorium oxide can be prepared from it:

The thorium nitrate is dissolved in water. Ammonium hydroxide added to this solution forms a precipitate of thorium hydroxide. This precipitate is washed several times by decantation, and then dissolved in nitric acid. By repeating this cycle several times a solution of thorium nitrate can be obtained practically free of sulphate. Oxalic acid is then added to this solution to precipitate thorium oxalate. This precipitate is filtered off, washed, dried, and ignited in a muffle furnace at about 900° C. to form thorium oxide.

### 1. CRUCIBLES OF UNFUSED THORIUM OXIDE

Thorium oxide was used at the National Bureau of Standards as a crucible material at first in the unfused form.[8] The powdered thorium oxide was tamped into the form of a crucible and then heated to about 1,800° C. This heating sintered the oxide to some extent. It was found that when using the crucibles for melting platinum in the high-frequency induction furnace, further sintering of the crucible with consequent shrinkage took place and cracks developed large enough to let molten metal through.

It is not always feasible to precalcine a crucible to a temperature higher than that at which it is to be used, nor is it practicable to cast a crucible from a molten mass of these high melting-point refractories. However, if it is possible to fuse the refractory oxide as a preliminary step, a crucible tamped from the fused and ground

[7] Louis Jordan and William H. Swanger, The Properties of Pure Nickel, B. S. Jour. Research, 5, (RP257). December, 1930.

[8] R. P. Neville, The Preparation of Platinum and of Platinum-Rhodium Alloys for Thermocouples, Trans. Am. Electrochem. Soc., 43, p. 371; 1923.

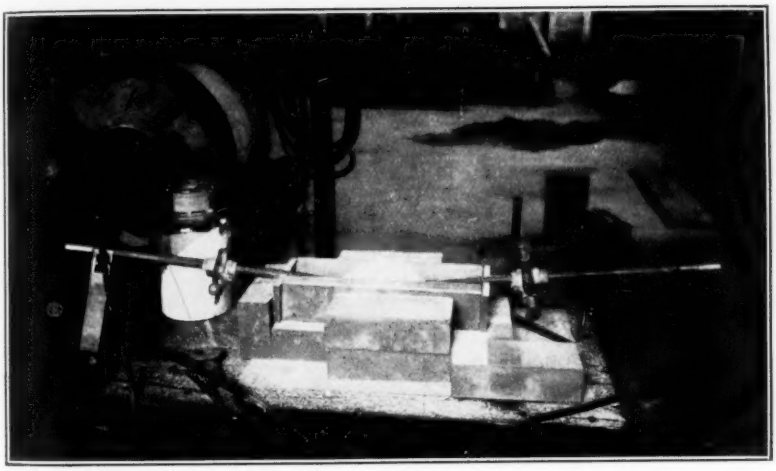

FIGURE 1.—*Furnace for fusing thorium oxide*

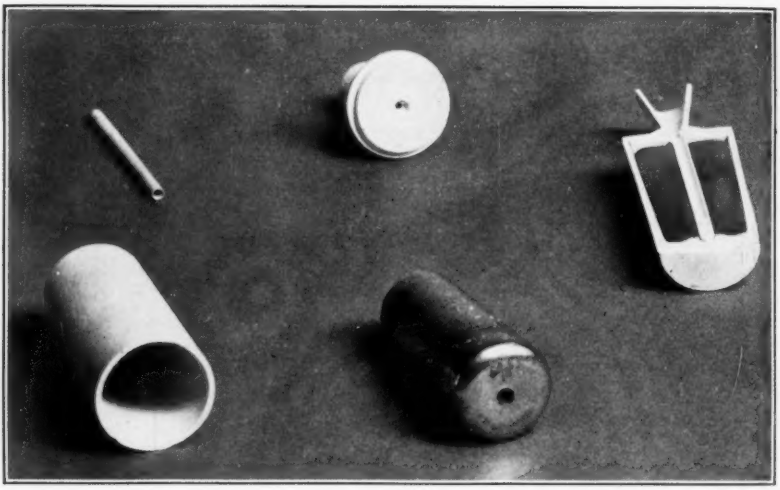

FIGURE 3.—*Crucible and ingot as used in the determination of melting or freezing points*

oxide will not shrink a great deal when heated even to temperatures just short of its melting point. It is true that such crucibles may, from nonuniform heating, develop cracks due to unequal thermal expansion, but if the crucible is properly backed up with refractory material these cracks do not open sufficiently to let molten metal through.

### 2. PROCEDURE FOR FUSING THORIUM OXIDE

The melting point of thorium oxide is so high that the temperature of the carbon arc is required to fuse it. However, if the oxide is fed into the ordinary carbon arc the thoria becomes contaminated with carbon. If, however, oxygen is also fed into the arc the formation of carbide can be almost entirely prevented.

The method as developed by Fairchild and Peters [9] for accomplishing this is, briefly, as follows:

The furnace, Figures 1 and 2, consists of a box about 35 cm long, 15 cm wide, and 10 cm deep, open at the top, made up of loose plates

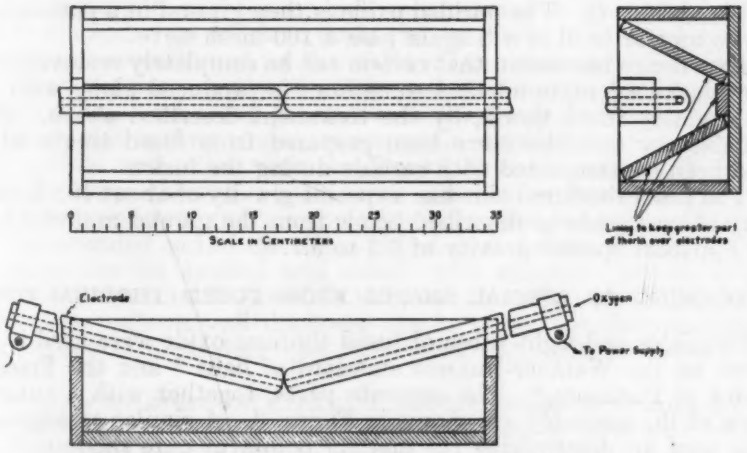


FIGURE 2.—*Drawing of furnace for fusing thorium oxide*

of pure graphite 1 cm thick laid on insulating bricks. The electrodes are two pure graphite rods 2 cm in diameter, 60 cm long, having holes 5 mm in diameter drilled through them lengthwise. They are placed over the long axis of the graphite box with the ends meeting at the center of the box and about 2 cm above the bottom. The tops of the ends of the box are cut away somewhat at the middle to allow the electrodes to lie more nearly horizontally without short circuiting against the box.

Before striking the arc, unfused thorium oxide is heaped over the junction of the two electrodes in a pile about 10 cm deep and a fairly rapid stream of oxygen is fed through the holes in the electrodes to maintain an oxidizing atmosphere around the arc. When the arc is struck the thorium oxide near the electrodes begins to fuse. It is necessary occasionally to push the unfused thorium oxide into the arc,

[9] C. O. Fairchild and M. F. Peters, U. S. Patent No. 1545951; July 14, 1925.

keeping it covered as much as possible. This may be done with a graphite rod. A 220-volt a. c. arc drawing approximately 200 amperes with about one-half ohm resistance in series with the arc has been used for this purpose.

After a pool of fused material has formed between the electrodes and the power has been cut off, the frozen thoria "glass" is picked out and the unfused particles adhering to it are knocked off. The fused thorium oxide has a glassy appearance generally with a pinkish tint which has been attributed by some to the presence of small amounts of rare earth impurities. Occasionally blackened particles apparently contaminated with carbon are found in the mass. These are picked out and treated separately. The unfused material is again heaped over the electrodes and the operation repeated.

The fused thorium oxide is ground in a steel ball mill with steel balls until all of the oxide will pass a 100-mesh sieve. The ground material is then thoroughly leached with hydrochloric acid to remove the iron introduced during the grinding and to decompose any carbides present, after which it is washed, dried, and ignited in a muffle at about 900° C. The purified oxide is then ground in a porcelain or agate mortar until it will again pass a 100-mesh sieve.

Experience has shown that carbon can be completely removed from the blackened material that sometimes is produced along with the clear glassy fused thoria, by the treatment described above. Very satisfactory crucibles have been prepared from fused thoria which had been contaminated with carbide during the fusion.

The fused thorium oxide has a specific gravity of about 10. Refractory shapes made as described below from the ground material have an apparent specific gravity of 9.5 to 9.7.

### 3. FORMING OF SPECIAL SHAPES FROM FUSED THORIUM OXIDE

Crucibles and sight tubes of fused thorium oxide were used in the work on the Waidner-Burgess standard of light [10] and the Freezing Point of Platinum.[11] The separate parts, together with a cutaway view of the assembly are shown in Figure 3. A similar arrangement was used for determining the melting points of pure rhodium [12] and of some platinum-rhodium alloys.

The method of making thoria crucibles is as follows: The thorium oxide, mixed with just enough of a bonding solution to dampen it slightly is tamped into a graphite mold by means of a chisel-pointed tamping tool. The bonding solution used contains 1 g of thorium chloride ($ThCl_4$) in 5 ml of solution. The solid plug of thorium oxide thus formed in the graphite mold is drilled while the material is still damp to form a crucible in the mold of the desired wall thickness. Crucibles having walls as thin as 1 mm have been made in this manner with a relatively small proportion of breakages.

The firing of these crucibles is done in two stages. The first stage or preliminary firing, to harden and shrink the crucible enough so that it may be removed from the mold and handled, is done by inclosing the mold containing the crucible, previously dried, in another graphite

[10] H. T. Wensel, William F. Roeser, L. E. Barbrow, and F. R. Caldwell, The Waidner-Burgess Standard of Light, B. S. Jour. Research **6**, (RP 325); 1931.
[11] William F. Roeser, F. R. Caldwell, and H. T. Wensel, The Freezing Point of Platinum, B. S. Jour. Research, **6**, RP 326; 1931.
[12] William H. Swanger, Melting, Mechanical Working, and Some Physical Properties of Rhodium, B. S. Jour. Research, **3**, (RP127); December, 1929.

shell and heating in air to 1,100° or 1,200° C. The purpose of the outer shell is to protect the graphite mold from burning when heated in air.

When heated in contact with carbon to temperatures much above 1,200° C. thorium oxide and zirconium oxide react with carbon to form carbides. Consequently it is not possible to complete the firing of crucibles of these materials in the graphite molds in which they were formed.

After the preliminary firing the crucibles are removed from the graphite molds and are then heated to a higher temperature, 1,700° or 1,800° C. The crucibles are kept out of direct contact with graphite during the firing. In case the Arsem or induction furnaces are used this may be done by supporting them on a tungsten or molybdenum sheet or a block of refractory material, such as magnesium oxide or zirconium silicate.

The materials used for crucibles are also used in making sight tubes. Instead of using a relatively dry mixture, however, sufficient thorium chloride solution is added to make a thick paste. A highly polished brass rod, slightly tapered, and rounded at the small end is used as a mandrel on which to make the sight tube. The rod should be of the diameter desired for the inside of the sight tube. A suitable amount of the paste is placed on the rod near the rounded end and molded around and along the rod with the fingers. The rod, with the paste on it is then placed on a smooth, unpainted, close grained wood surface and rolled with the fingers, thus spreading the paste uniformly along the rod, at the same time drying it somewhat. If the correct consistency of the paste has been used the tube will close over the rounded end of the rod. If it does not close, a little of the wet paste can be applied and rolled until smooth. Immediately after rolling the tube it should be removed from the rod. A tube of surprisingly uniform wall thickness can be made, the thickness and length, of course, depending upon the amount and initial consistency of the paste.

The tubes are dried and fired in a manner similar to that used for the crucibles, except that the preliminary firing is dispensed with. For convenience in firing, the tubes are set upright in holes drilled in a block of thorium oxide.

Crucible covers and cones, as shown in Figure 3, are made in the same way as the crucibles. The cones are cemented to the covers with a thin paste of thorium oxide-thorium chloride solution after the preliminary firing. After the metal to be melted has been put into the crucible the separate parts are assembled as shown in Figure 3 and cemented together with a thinner paste of the same materials.

The platinum used in the work on the Waidner-Burgess standard of light [13] and the freezing point of platinum [14] was melted more than 150 times in a thorium-oxide crucible such as just described. The degree of contamination of the platinum by the thorium-oxide crucible may be inferred from the discussion of this point given in the paper referred to previously.[15]

Another method used in making crucibles of fused thorium oxide is to tamp and press the crucible material into a steel mold. A line

[13] See footnote 10, p. 1136.
[14] See footnote 11, p. 1136.
[15] See footnote 10, p. 1136.

sketch of a cross section of such a mold is shown in Figure 4. After this mold had had some use the walls were polished to a mirror finish and plated with chromium. It was found that there was appreciably

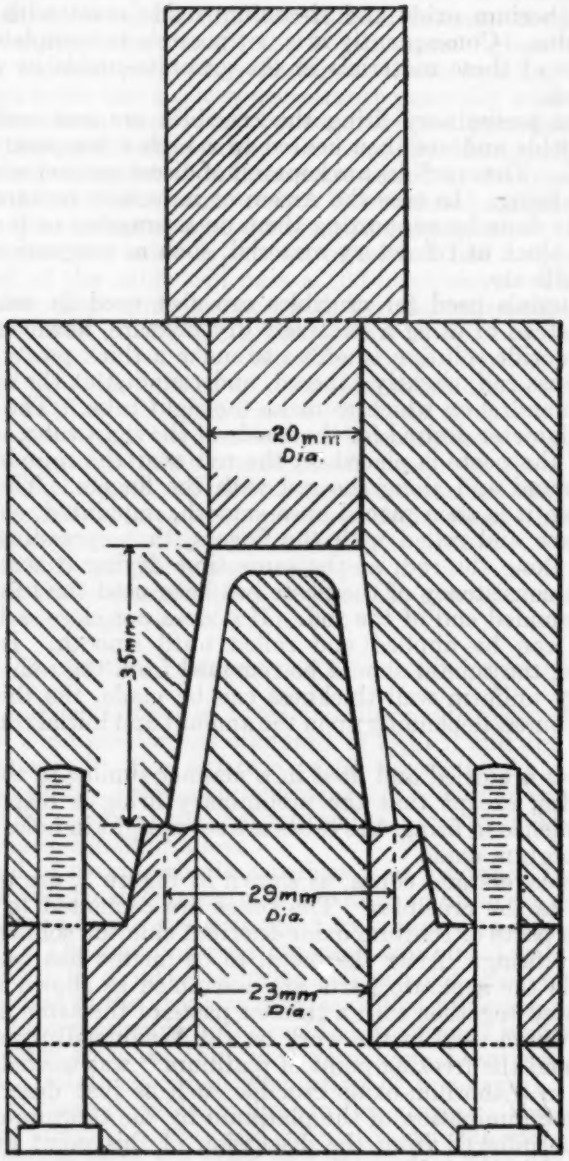


FIGURE 4.—*Cross section of steel mold (assembled*

less adherence of the thorium oxide to the chromium surface than to the steel surface.

Satisfactory crucibles are obtained with this steel mold when the amount of material for each crucible is controlled to within 0.5 g and

the amount of bonding solution to within 0.1 ml. It requires 62.5 g of fused thorium oxide and 2.2 ml of thorium-chloride solution, prepared as described above, to form a crucible in this mold. The capacity of the crucible is 7 $cm^3$.

The crucibles after removal from the mold are dried and then fired to about 1,800° C.

## IV. MAGNESIUM OXIDE

### 1. COMMERCIAL FUSED MAGNESIUM OXIDE

Crucibles of fused magnesium oxide can be used at temperatures considerably above that at which the crucibles have been fired without trouble due to shrinkage. This material is available commercially, ground to sizes suitable for hand tamping of the crucibles. The electrically fused or sintered magnesium oxide ground to 60 mesh and finer is moistened with a water solution of magnesium chloride before tamping. This solution is made up by dissolving an amount of magnesium chloride ($MgCl_2.6H_2O$) equal to 2 per cent of the weight of the magnesium oxide needed for the crucible in a minimum amount of water. This solution is added to the batch of refractory, together with just enough additional water to moisten the refractory so that it may be tamped into the crucible mold. Emphasis is placed on the use of a chisel-pointed tool for tamping. By this means, the "rings" marking the successive additions of ground refractory may be avoided.

It is convenient to form crucibles of magnesium oxide in graphite molds or shells, because magnesium oxide does not combine with carbon to form carbides and the crucibles can be heated to 1,800° C. while held in the molds in which they were formed.

Such crucibles may also be tamped in pasteboard cylinders such as the ordinary mailing tubes or cases. In firing the crucibles the paper cases are allowed to burn away. Ordinarily a wood or metal mandrel is used as a core around which the crucible is formed and is, of course, removed before the crucible is fired.

### 2. CHEMICAL REAGENT GRADE OF MAGNESIUM OXIDE

The commercial fused magnesium oxide is not of sufficient purity for use with pure metals, as was found in previous work at the National Bureau of Standards.[16] The more pure "C. P." or chemical reagent grade of unfused magnesium oxide can be sintered to form very hard and dense crucibles that have almost a porcelainlike body or texture. This oxide is a very light and fluffy powder and shrinks to about half its original volume when heated to 1,600° to 1,800° C. Consequently it is necessary to calcine the powder before forming a crucible. For this purpose it may be lightly tamped into a convenient graphite shell, preferably around a small core or mandrel, or pressed into briquets. A small amount of alcohol or petroleum ether mixed with the powder improves its tamping properties. The uncalcined powder which has been exposed to the air for some time contains about 2.5 per cent of carbon dioxide. It is advisable to remove

[16] See footnote 1, p. 1132.

this by heating in an ordinary muffle to about 900° C. before attempting the calcination at the higher temperature, especially if the latter heating is to be done in the Arsem furnace; otherwise the sudden evolution of carbon dioxide at the reduced pressure of the Arsem furnace may blow the oxide out of its container.

The calcined oxide is broken up and ground in a porcelain ball mill to pass a 100-mesh screen. This material is mixed with a 2 per cent solution of magnesium chloride (2 g $MgCl_2.6H_2O$ in 100 ml $H_2O$) which is more dilute than the bonding solution used with the fused magnesium oxide. Only enough of this solution is used to moisten the oxide so that it can be tamped. The crucibles are most conveniently made by tamping them in graphite molds of the required shape and then firing them in the same mold to 1,600° to 1,800° C. If the preliminary calcining of the oxide was carried to about 1,700 °C. and the tamping was well done, the linear shrinkage of these crucibles during the final firing is about 4 per cent.

Crucibles of this previously calcined "C. P." magnesium oxide are also made in the steel mold described above under "Thorium oxide crucibles." The same precautions as to tamping and accurate measuring of the quantity of refractory and of bonding solution apply. Generally, it requires 21.5 to 22.0 g of the previously calcined magnesium oxide and 2.0 ml of the 2 per cent magnesium chloride solution to fill the mold. The amount of oxide varies slightly according to the temperature at which it was calcined; that is, the higher the temperature the denser the material becomes. The apparent specific gravity of these "pure" magnesium oxide crucibles is about 3.5. The specific gravity of fused magnesia is generally given as 3.5. to 3.7.

Crucibles of this purer grade of magnesium oxide have been used at the National Bureau of Standards for melting pure metals, such as iron, nickel, gold, platinum, and platinum-rhodium alloys, without appreciable contamination of the metals by the refractory. It has been found that platinum melted in vacuo (pressure of 1 to 2 mm of mercury) in a crucible of this type gave a thermal electromotive force against the bureau's platinum standard, Pt 27, of +50 microvolts at 1,200° C. Samples from the same lot of platinum melted in such a crucible open to the air gave a thermal electromotive force of +6 to +10 microvolts against the standard at 1,200° C. Spectrographic examination showed the presence of magnesium in the vacuum melted platinum and its absence from the platinum melted in a similar crucible open to the atmosphere. It has not yet been established whether the magnesium in the platinum was a product of the dissociation of magnesium oxide at the high temperature and low pressure or the result of a reducing action of oil vapors from the vacuum pump on the hot magnesium oxide.

## V. ZIRCONIUM OXIDE

### 1. "SLIP-CAST" CRUCIBLES

Crucibles of fused zirconium oxide for the melting of platinum and platinum-rhodium alloys are made essentially as described in a previous report.[17] Briefly, the method is as follows: Commercial electrically fused or sintered zirconia, ground to about 100-mesh and

[17] See footnote 1, p. 1132.

finer, is first washed with hydrochloric acid to remove iron and then roasted in an open muffle at about 800° to 900° C. to remove carbon. A casting "slip" is then prepared by grinding for about eight hours in a porcelain ball mill with flint pebbles, a batch of the following proportions: 1,000 g purified zirconia, 40 g china clay, and 500 ml water. Crucibles are formed by pouring this slip into plaster of Paris molds. As water is absorbed from the slip into the walls of the mold, the mold is kept filled with more of the slip. When sufficient solid has formed on the inside wall of the mold the excess slip is poured out. The cast form continues to shrink and soon can be removed from the mold. It is then dried, first in the air, then in an oven at 120° to 150° C. and finally fired to about 1,700° C., keeping in mind that the crucibles must be kept from direct contact with graphite at temperatures above about 1,200° C.

The linear shrinkage of these slip-cast crucibles is about one-third. About half of this shrinkage takes place during the drying and the remainder during firing. Consequently the loss due to cracking is considerable.

### 2. TAMPED AND PRESSED CRUCIBLES

By tamping the purified zirconium oxide in graphite molds, or by tamping and pressing in a steel mold, crucibles may be made with a smaller proportion of losses from cracking. If made in a graphite mold, the crucibles can not be fired in the mold beyond 1,200° C. After a preliminary firing at this temperature they are removed from the mold and fired to about 1,700° C., in the same manner as the "slip-cast" crucibles. China clay is not added to the zirconium oxide in this method, but a solution of zirconium chloride (2 g $ZrCl_4$ in 100 ml water) may be used to moisten the zirconium oxide and act as a binder. (Thorium chloride and magnesium chloride solutions of similar concentration apparently serve equally well as binders.) The linear shrinkage of the tamped crucibles is about the same as that of the magnesuim oxide crucibles described above, viz, about 4 per cent. They are as hard and strong as the slip-cast zirconia crucibles and have been used at somewhat higher temperatures without softening, since no clay was used to bond them.

The commercial fused or sintered zirconium oxide contains a small amount of silica and more silica is introduced by the china clay in preparing the "casting-slip." The silica does not affect the purity of platinum melted in the cast crucibles when the melting is done in air, but does contaminate the platinum very severely when the melting is done in vacuo.

## VI. BERYLLIUM OXIDE

Pure beryllium oxide is not produced commercially. Through the courtesy of the Brush Laboratories (Inc.), of Cleveland, Ohio, a small quantity was supplied to the National Bureau of Standards, sufficient to permit a few observations to be made of its behavior as a refractory material. The oxide was apparently of high purity, very light and fluffy and very white. It was heated in a graphite container in the Arsem furnace to about 1,700° C, and in the high-frequency induction furnace to about 1,800° C. Like magnesium oxide, it does not combine with carbon at high temperatures to form carbides. It appeared to volatilize less rapidly than magnesium oxide under these

conditions. Like the "C. P." grade of magnesium oxide, it shrank to about half its original volume when calcined in graphite at 1,700° to 1,800° C.

The calcined beryllium oxide was broken up and ground to pass a 100-mesh screen. Several crucibles were tamped and pressed in the steel mold arleady described. A solution of beryllium chloride (4g $BeCl_2$ in 100 ml water) was used to moisten the beryllium oxide. The crucibles were fired in an Arsem furnace to 1,700° C. They were beautifully white, extremely strong and hard, and very resistant to thermal shock. The apparent specific gravity of the crucibles was about 3.0.

A melt of pure platinum was made in one of these crucibles in the high-frequency induction furnace. The metal was allowed to freeze in the crucible, and after removal of the button, except for a layer of volatilized platinum on the wall, it could hardly be seen that the crucible had been used.

Pure platinum melted in a beryllium oxide crucible in vacuo (pressure of 1 to 2 mm of Hg) proved to have alloyed with beryllium, a result similar to that obtained when using a magnesium oxide crucible. The vacuum-melted platinum gave a thermal electromotive force of +50 microvolts against the platinum standard, Pt 27, at 1,200° C. Spectrographic examination of the platinum disclosed the presence of beryllium. Another sample from this same lot of purified platinum sponge melted in air in a zirconium oxide crucible gave a thermal electromotive force of +4 microvolts to the platinum standard, Pt 27. The sample melted in air in the beryllium oxide crucible gave a thermal electromotive force of −7 microvolts against the standard.

Actual determinations of the amounts of thorium, magnesium, or beryllium introduced into pure platinum when melted in vacuo in crucibles of thorium, magnesium, or beryllium oxides, respectively, have not been made.

## VII. SUMMARY

1. The oxides of thorium, magnesium, zirconium, and beryllium can be used as refractories in which to melt metals of the highest purity without detrimental contamination of the metal by the refractory.

2. Thorium oxide is the most refractory of these four oxides. Its melting point has not been determined, but is generally believed to be above 3,000° C. The oxide is fused in the carbon arc, oxygen being fed into the arc to prevent the formation of thorium carbide. Crucibles prepared from this fused material have been used at temperatures to 2,200° C.

3. Magnesium oxide volatilizes rapidly at temperatures between 2,000° C. and its melting point (2,800° C.), especially under reduced pressure or in contact with carbon. Crucibles of magnesium oxide have been used at temperatures up to 1,800° C.

4. Crucibles of commercial zirconium oxide containing a small amount of silica are used only under oxidizing conditions and at atmospheric pressure, but are safely used under these conditions at temperatures up to 2,000° C.

5. A few experiments with beryllium oxide indicate that it does not volatilize as rapidly in contact with carbon at 2,000° C. as does magnesium oxide, and that very satisfactory crucibles for high-temperature service may be formed from it.

6. Crucibles of any of the four oxides may be formed by tamping and pressing in a steel mold. Special shapes are made by tamping the refractory into graphite molds. Crucibles of zirconium oxide were made by casting a "slip" into plaster of Paris molds.

7. The crucibles may be fired at 1,600° to 1,800° C. in an Arsem furnace. Magnesium and beryllium oxides do not form carbides when heated to these temperatures in contact with carbon. Thorium and zirconium oxides must be kept out of direct contact with carbon at temperatures above 1,200° C.

WASHINGTON, June 30, 1930.

# THE OXIDATION OF SUGARS. I. THE ELECTROLYTIC OXIDATION OF ALDOSE SUGARS IN THE PRESENCE OF A BROMIDE AND CALCIUM CARBONATE

By Horace S. Isbell and Harriet L. Frush

ABSTRACT

A new method has been devised for the preparation of calcium salts of the sugar acids in which the sugar is electrolytically oxidized in the presence of calcium carbonate and a bromide. The sugar is oxidized in manner analogous to the well-known bromine oxidation, but since only a small quantity of bromide is used as a catalyst, the new method has the decided advantage that the reaction product does not contain any objectionable substances derived from the oxidant. On account of this, the separation of the product is greatly simplified, as shown by the fact that calcium gluconate, galactonate, mannonate, rhamnonate, and arabonate are easily crystallized on evaporation of the solutions resulting from the oxidation of the respective sugars. The preparation of the calcium salts of xylonic, lactobionic, and maltobionic acids is also given.

The raw materials, with the exception of the bromide, which is used only in small quantities as a catalyst, are relatively cheap. This fact, in conjunction with the high current efficiency and high yield, should make the method of considerable commercial value for the preparation of calcium gluconate and related products.

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## I. INTRODUCTION

The widespread interest in the use of calcium gluconate for the medical treatment of calcium deficiency makes the discovery of an improved method for its preparation of unusual importance. The study of the oxidation of aldose sugars in the presence of various buffers was begun by C. S. Hudson and the senior author several years ago. The early work was largely confined to the study of bromine oxidation in the presence of different buffers. A very convenient method for the laboratory preparation of the monocarboxylic sugar acids was developed.[1] However, this method, as well as the other methods heretofore used, is not wholly satisfactory for the commercial manufacture of sugar acids or their salts. For if oxidation is effected by bromine [2] or by chlorine [3] two molecules of hydrogen

[1] Hudson and Isbell, B. S. Jour. Research, 3, p. 57, (RP82); 1929; also J. Am. Chem. Soc., 51, p. 2225; 1929.
[2] Kiliani and Kleemann, Ber., 17, p. 1296; 1884.
[3] Stoll and Kussmaul, U. S. Patent 1648368; 1927.

bromide or hydrogen chloride are formed for each molecule of sugar which is converted to the acid. This large amount of hydrogen bromide decreases the reaction rate. This retarding effect may be eliminated by the addition of a base or buffer, such as calcium carbonate,[4] but even then a large quantity of calcium bromide is formed, which seriously interferes with the separation of the desired product. The fermentation method[5] for the preparation of calcium gluconate does not have the objectionable features just mentioned, but it does not give a quantitative yield, and requires careful control lest foreign organisms enter the vats and produce undesirable side reactions.

Electrolytic oxidations are not only cheap and convenient, but they have, in addition, the decided advantage that no undesirable substances are produced from the oxidant. By the usual electrolytic oxidation, the aldose sugars are not oxidized in appreciable quantity to the corresponding aldonic acids. Thus, Löb [6] found that glucose on electrolytic oxidation gives a whole series of degradation products, including *d*-arabinose and formaldehyde.

## II. A NEW PROCESS FOR THE MANUFACTURE OF CALCIUM GLUCONATE AND SIMILAR PRODUCTS

The undesirable features of the older methods for the preparation of sugar acids have been overcome by a new process wherein oxidation is effected electrolytically in the presence of a small quantity of a bromide. As a result, a nearly quantitative oxidation of the sugar into its monocarboxylic acid is obtained without objectionable by-products. In the preparation of calcium salts the oxidation is conveniently conducted in the presence of the bromide and calcium carbonate. The calcium carbonate reacts with the sugar acid as fast as it is formed and thus maintains a nearly neutral solution in which the bromine is absorbed as fast as it is liberated by electrolysis. The total reaction is represented by the following equation:

$$2\,C_6H_{12}O_6 + CaCO_3 + NaBr + H_2O \xrightarrow{\text{electrolysis}} 4\,F \rightarrow Ca\,(C_6H_{11}O_7)_2 + 2H_2 + CO_2 + NaBr$$

Many of the calcium salts of the sugar acids crystallize very readily from water solution. Thus, when a concentrated solution of glucose is oxidized in the manner outlined, calcium gluconate crystallizes from the solution toward the end of the reaction. This may be separated by filtration, after which additional glucose and calcium carbonate may be added to the mother liquor and the process repeated. The bromide is thus recovered in the mother liquors; hence a small amount of it will effect the oxidation of an indefinitely large amount of sugar. The only bromide which is lost is that which contaminates the product and even this bromide may be largely recovered from the mother liquors from a second crystallization. In addition to expediting the desired reaction the bromide causes an increase in the conductivity of the solution, thus reducing the resistance and hence the amount of energy wasted as heat. The quantity of bromide used in

[4] Clowes and Tollens, Ann., **310**, p. 166; 1900.
[5] May, Herrick, Moyer, and Hellbach, Ind. Eng. Chem., **21**, p. 1198; 1929.
[6] Löb, Biochem. Z., **17**, pp. 132, 343; 1909.

the experimental work reported in this publication is more than the minimum amount required for a smooth reaction. The optimum quantity for use in the commercial preparation of these derivatives depends on many factors, including the economic aspects of the subject which will not be considered in this publication.

The oxidation of 1 mol of an aldose sugar to the corresponding acid requires 1 atom of oxygen or 2 Faradays. The actual quantity of electricity required for the oxidations is very near this amount. Thus 45 g (0.25 mol) of glucose is oxidized to the extent of 95 per cent by 0.5 Faraday (13.4 ampere-hours). The fact that two equivalents of electricity cause the disappearance of 95 per cent of the reducing power of the sugar (Scales method) shows that the principal reaction is the oxidation of the sugar to the corresponding acid, because any other oxidation reaction which would decrease the reducing power of the solution to the same extent would require several equivalents of electricity.

The high current efficiency, together with the low potential required, makes the process very economical. The cost for the electricity used in the oxidation is extremely small as compared with the cost of bromine or even chlorine as an oxidizing agent. The yield of the final product is nearly quantitative; in fact, as high a yield may be obtained as may be obtained by the use of expensive reagents.

## III. EXPERIMENTAL DETAILS

### 1. APPARATUS AND METHOD USED

A very simple electrolytic cell was used. This consisted of two electrodes fitted in a 2-liter three necks Pyrex distilling flask which was equipped with a mechanical stirrer. The electrodes consisted of round graphite rods 22 mm in diameter and sufficiently long to reach the bottom of the flask. They were placed in the outer necks of the flask as illustrated in Figure 1, while the stirrer was inserted in the center. The sugar solution containing the bromide, and calcium carbonate in suspension, was placed in the flask and a direct current was passed between the electrodes. A potential of 15 volts gave a current of slightly more than 0.5 ampere, or a current density of 10 amperes per square decimeter. The potential is considerably more than that required for the actual oxidation, the loss being largely due to the resistance of the electrodes and of the solution. The quantity of electricity was measured by a copper coulometer in series with the oxidation cell. As the reaction proceeded, hydrogen and carbon dioxide escaped from the flask. The reaction mixture remained only slightly acid, and colorless, the bromine being absorbed as fast as it was liberated. Samples were taken at intervals and the reducing sugar was determined by copper reduction or iodine titration. The samples were also tested for the presence of free bromine with potassium iodide and starch. In all cases negative tests for free bromine were obtained until the reaction was nearly complete, as indicated by only a faint Fehling's test for reducing sugar. The completion of the reaction could be detected directly by the appearance of a faint yellow coloration which occurred when slightly more than the theoretical quantity of current had been used. At the end of the reaction the sugar was nearly completely converted into the calcium salt of the

corresponding monobasic acid. The previously known calcium salts of gluconic,[7] mannonic,[8] galactonic,[9] arabonic,[10] and rhamnonic [11] acids were prepared by simple evaporation of the solutions and crystallization of the products. The mother liquors may be used in subsequent oxidations, thus giving a very efficient method for the conversion of the sugars into salts of the sugar acids. Xylonic, maltobionic, and

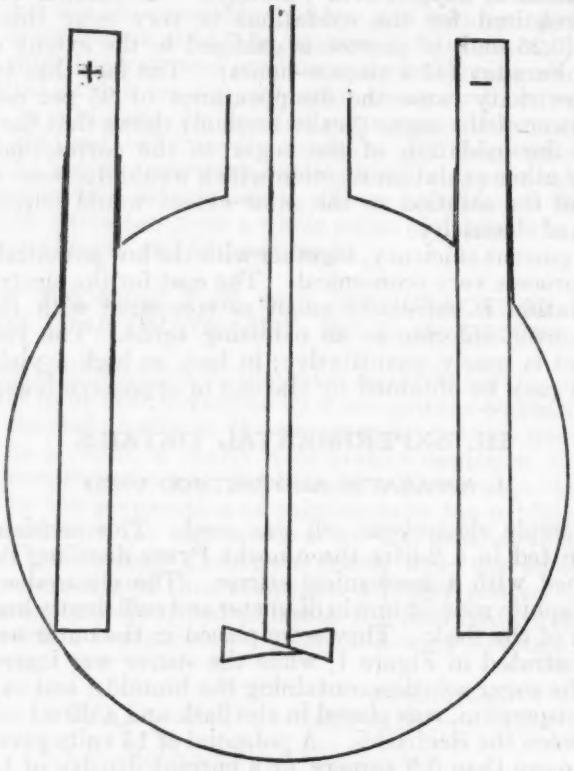


FIGURE 1.—*Oxidation cell*

lactobionic acids were separated by the formation of insoluble basic calcium salts.[12] These salts may be used for the preparation of any desired derivative.

## 2. OXIDATIONS OF *d*-GLUCOSE, *d*-GALACTOSE, AND *d*-MANNOSE

A solution consisting of 45 g of anhydrous *d*-glucose (0.25 mol) and 8 g of calcium bromide (anhydrous) in sufficient water to give 1 liter was placed with 25 g of calcium carbonate in the apparatus illustrated in Figure 1. A direct current of 0.5 ampere was passed through the solution and the quantity of electricity was measured with a copper coulometer. Samples of the solution were taken from

[7] Fischer, Ber., **23**, p. 2614; 1890.
[8] Fischer and Hirschberger, Ber., **22**, p. 3220; 1889.
[9] Schnelle and Tollens, Ann., **271**, p. 81; 1892.
[10] Kiliani, Ber., **19**, p. 3029; 1886.
[11] Rayman, Ber., **21**, p. 2046; 1888.
[12] Hudson and Isbell, B. S. Jour. Research, **3** (RP82), p. 00; 1929.

time to time, and the amount of sugar remaining in the solution was determined by Scales [13] method. The difference between the amount of sugar at the beginning of the reaction and at any given time is equal to the amount of sugar oxidized. The results are shown in Figure 2. The amount of oxidation is nearly proportional to the quantity of current used, and the oxidation is virtually complete when the theoretical quantity (13.4 ampere-hours) of electricity has passed through the solution. Qualitative tests for free bromine on small portions of the solution were negative until slightly more than the theoretical amount of current had been used, after which positive tests were obtained. The tests were made with potassium iodide and starch solution in the usual manner. An excess of bromine is slowly absorbed by the calcium salts of sugar acids, and hence the solutions

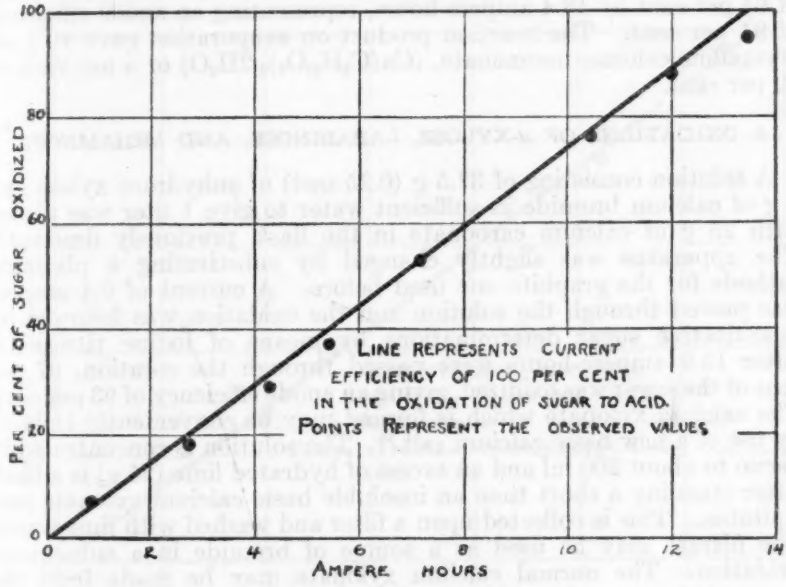


FIGURE 2.—*Oxidation of glucose*

were not allowed to stand more than two or three minutes before making the tests.

The current was interrupted when the sugar determination showed that 96 per cent of the sugar had been oxidized to the monobasic acid. The solution was filtered and then concentrated in vacuo to a thin sirup from which crystalline calcium gluconate was readily separated A total of 45 g of the salt, $Ca(C_6H_{11}O_7)_2.2H_2O$ was obtained, representing a yield of about 77 per cent of the theoretical. The calcium bromide in the mother liquors prevents the complete crystallization of the calcium gluconate, but the residual salt may be recovered in subsequent runs if additional sugar is added and the process repeated. However, if it is desired to recover the maximum quantity of calcium gluconate the calcium bromide may be removed with silver oxalate.[14]

[13] Scales, J. Ind. Eng. Chem., **11**, p. 747; 1919.
[14] Isbell, B. S. Jour. Research, **5** (RP226), p. 753; 1930.

The solution thus freed from the calcium bromide gives additional calcium gluconate on evaporation.

The oxidation of galactose and of mannose was conducted in a manner analogous to that just outlined for glucose. The results were similar in that the sugars were virtually quantitatively converted into calcium salts of the corresponding sugar acids.

Forty-five grams (0.25 mol) of *d*-galactose was oxidized to the extent of 98 per cent by 13.3 ampere-hours representing an anode efficiency of 99 per cent. The reaction product on evaporation gave 35 g of crystalline calcium galactonate, $(Ca(C_6H_{11}O_7)_2.5H_2O)$ which represents a net yield of 54 per cent. The residual calcium galactonate could be obtained only after removing the calcium bromide from the mother liquors.

Forty-five grams (0.25 mol) of *d*-mannose was oxidized to the extent of 94 per cent by 13.4 ampere-hours, representing an anode efficiency of 94 per cent. The reaction product on evaporation gave 40 g. of crystalline calcium mannonate, $(Ca(C_6H_{11}O_7)_2.2H_2O)$ or a net yield of 69 per cent.

### 3. OXIDATIONS OF *d*-XYLOSE, *l*-ARABINOSE, AND *l*-RHAMNOSE

A solution consisting of 37.5 g (0.25 mol) of anhydrous xylose and 8 g of calcium bromide in sufficient water to give 1 liter was placed with 25 g of calcium carbonate in the flask previously described. The apparatus was slightly changed by substituting a platinum cathode for the graphite one used before. A current of 0.4 ampere was passed through the solution and the oxidation was followed by quantitative sugar determinations by means of iodine titration.[15] After 13.9 ampere-hours were passed through the solution, 97 per cent of the sugar was oxidized, giving an anode efficiency of 93 per cent. The calcium xylonate which is formed may be conveniently isolated by use of a new basic calcium salt.[16] The solution is concentrated in vacuo to about 200 ml and an excess of hydrated lime (25 g) is added. After standing a short time an insoluble basic calcium xylonate precipitates. This is collected upon a filter and washed with lime water. The filtrate may be used as a source of bromide in a subsequent oxidation. The normal calcium xylonate may be made from the basic salt by removing the excess of lime with carbon dioxide. After filtration and evaporation of the aqueous solution a thick sirup is obtained which may be reduced to an amorphous powder by drying.

The following experiment shows that as the oxidation of the sugar progresses more sugar may be added to replace that which is converted to the calcium salt, and thus build up the concentration of the desired product. In the case of xylose the calcium xylonate is very soluble, and hence it does not crystallize from the solution. But with glucose, crystalline calcium gluconate forms which may be separated by filtration from time to time and the process continued.

Fifty-seven grams of xylose and 15 g of sodium bromide dissolved in 1,500 ml of water were placed in the oxidation flask with 37 g of calcium carbonate. Electrolytic oxidation was conducted with a current of 0.3 ampere. At intervals of 21 ampere-hours four additional portions of xylose (57 g each) and calcium carbonate (20 g each)

[15] Kline and Acree, B. S. Jour. Research, 5 (RP247), p. 1063; 1930.

[16] The composition of this salt, as well as the composition of the corresponding salts of maltose and lactose, is being investigated.

were added. After 109 ampere-hours oxidation was nearly complete, only 3 per cent of the 285 g of xylose remained in the solution, representing an anode efficiency of 91 per cent.

The oxidation of *l*-arabinose and of *l*-rhamnose was conducted in a slightly smaller apparatus than that employed in the experiments on glucose and galactose, but essentially the same conditions were maintained except that both electrodes were of platinum instead of graphite. The quantities of the reagents were one-half those used in the first xylose experiment.

An 18.75 g (0.125 mol) sample of *l*-arabinose was oxidized to the extent of 91 per cent by 8.0 ampere-hours of current. The reaction product on evaporation gave 14 g, or a net yield of 49 per cent, crystalline calcium arabonate ($Ca(C_5H_9O_6)_2.5H_2O$). The anode efficiency (76 per cent) was not as high as that obtained with some of

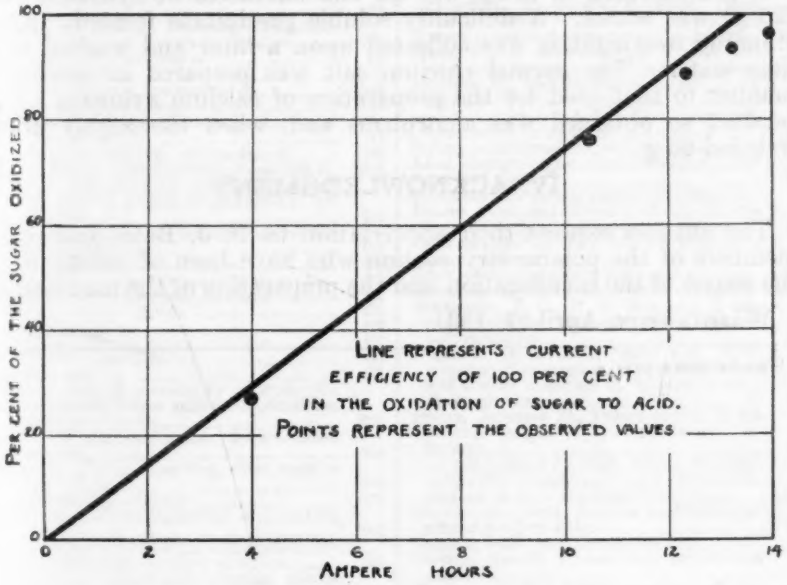


FIGURE 3.—*Oxidation of lactose*

the other sugars. This was presumably due to the formation of an insoluble crust on the cathode which appears to be a basic calcium arabonate. This subject will be considered in a future publication.

An 18.75 g (0.103 mol) sample of *l*-rhamnose (monohydrate) was oxidized to the extent of 94 per cent by 6.4 ampere-hours, representing an anode efficiency of 81 per cent. The reaction product, on evaporation, gave 19 g of crude crystalline calcium rhamnonate.

### 4. OXIDATIONS OF *d*-LACTOSE AND *d*-MALTOSE

A solution consisting of 90 g (0.25 mol) of *d*-lactose (monohydrate) and 8 g of calcium bromide in sufficient water to give 1 liter was placed, together with 25 g of calcium carbonate, in the apparatus used for the oxidation of xylose. A current of 0.4 ampere was passed through the solution and the oxidation was followed by iodine titration of the unoxidized sugar. The results, shown in Figure 3, clearly

indicate that the reaction proceeded with the same regularity which characterized the oxidations of the monosaccharides. The use of calcium carbonate in the oxidation of the reducing disaccharides maintains a nearly neutral solution so that little or no hydrolysis of the disaccharides occurs. After the theoretical quantity of current had been consumed the reaction was about 95 per cent complete. The solution was treated with lime (25 g) and the product was obtained as the basic calcium lactobionate previously reported by C. S. Hudson [17] and the senior author.

The oxidation of *d*-maltose (monohydrate) was conducted in manner analogous to that given for lactose. After 13.9 ampere-hours, sugar determinations showed that 98 per cent of the sugar had been oxidized, with an anode efficiency of 94 per cent. The product was isolated by means of a new basic calcium maltobionate. The solution was concentrated to about 300 ml and an excess of hydrated lime (25 g) was added. A difficultly soluble precipitate formed. After standing overnight it was collected upon a filter and washed with lime water. The normal calcium salt was prepared in analogous manner to that used for the preparation of calcium xylonate. The product so obtained was amorphous and, when thoroughly dried, weighed 60 g.

## IV. ACKNOWLEDGMENT

The authors express their appreciation to F. J. Bates and other members of the polarimetry section who have been of assistance in the course of the investigation and the preparation of the manuscript.

WASHINGTON, April 27, 1931.

[17] See footnote 1, p. 1145.

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